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Rhenium *versus* cadmium: an alternative structure for a thermally stable cadmium carbonyl compound†

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An alternative description is provided for the previously reported novel tetranuclear cadmium carbonyl compound, $[Cd(CO)_3(C_6H_3Cl)]_4$. Specifically, consideration of single crystal X-ray diffraction data indicates that the compound is better formulated as the rhenium compound, $[Re(CO)_3(C_4N_2H_3S)]_4$. Furthermore, density functional theory calculations predict that, if it were to exist, $[Cd(CO)_3(C_6H_3Cl)]_4$ would have a very different structure to that reported. While it is well known that X-ray diffraction may not reliably distinguish between atoms of similar atomic number (*e.g.* N/C and Cl/S), it is not generally recognized that two atoms with very different atomic numbers could be misassigned. The misidentification of two elements as diverse as Re and Cd ($\Delta Z = 27$) is unexpected and serves as an important caveat for structure determinations.

Introduction

The early discoveries that carbon monoxide can coordinate to a metal center paved the way for many important industrial applications, as exemplified by the Monsanto acetic acid process and olefin hydroformylation.[1] This area of chemistry, however, has been dominated by transition metals, a fact that may be attributed to the stabilization of the M–CO interaction by π-backbonding due to the availability of occupied metal d orbitals.[2] As such, main group metals that are devoid of occupied valence d orbitals do not typically form stable metal carbonyl compounds.[3] For this reason, the report of a structurally characterized thermally stable cadmium carbonyl compound is of particular significance.[4] Therefore, we have investigated this issue and provide herein an alternative explanation for the proposed structure.

Results and discussion

We are currently interested in the use of main group metal compounds for catalytic conversions of organic carbonyl compounds. For example, we have employed zinc compounds as catalysts for the reduction of CO_2 to the formic acid and formaldehyde oxidation levels, and also the reduction of aldehydes and ketones.[5] In addition to CO_2 chemistry, zinc compounds also catalyze reactions involving CO, as illustrated by the fact that zinc oxide (and also Cu/ZnO) is a catalyst for the synthesis of methanol from CO and H_2.[6] As such, the interaction between CO and ZnO has been investigated by a variety of techniques, which include IR spectroscopy,[7,8] solid state ^{13}C NMR spectroscopy,[9,10] ultraviolet photoelectron spectroscopy,[11] and scanning tunneling microscopy.[12] Zinc carbonyl compounds have also been generated under matrix isolation conditions[13–15] and in the gas phase,[16] but there are no reports of such compounds that have been structurally characterized by X-ray diffraction. Cadmium carbonyl compounds have received even less attention than their zinc counterparts, and were first observed by IR spectroscopic studies in an argon matrix.[17,18] In view of the transient nature of these Group 12 metal carbonyl compounds, the report of the synthesis of a thermally stable cadmium carbonyl compound, $[Cd(CO)_3(C_6H_3Cl)]_4$,[4] which has been highlighted in a review,[19] would be considered to be an important advance, especially given the novel synthetic approach. Specifically, $[Cd(CO)_3(C_6H_3Cl)]_4$ was reported to be obtained *via* the reaction of an aqueous methanol solution of $Cd(O_2CCCl_3)_2$ with *o*-vanillin (Scheme 1), which was described as a green pathway since the formation of this carbonyl compound did not involve the use of carbon monoxide.

The formation of $[Cd(CO)_3(C_6H_3Cl)]_4$ from $Cd(O_2CCCl_3)_2$ and *o*-vanillin is an unusual transformation and was considered to involve two separate sequences (Scheme 2).[4] First, the carbonyl ligands were proposed to originate from decomposition of the trichloroacetate anion to give chloroform, which converted in sunlight to CO *via* phosgene. In turn, the chloroaryl ligands were proposed to derive by a sequence that involves: (i) initial oxidation of *o*-vanillin to *o*-vanillic acid, (ii) reaction of the *o*-vanillic acid with the aforementioned phosgene and CO to

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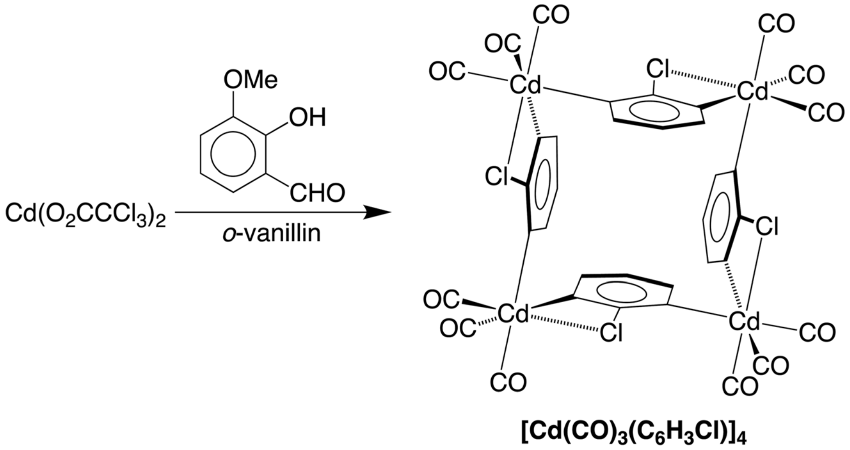
† Electronic supplementary information (ESI) available: Crystallographic data (CIFs), and Cartesian coordinates for geometry optimized structures. CCDC 2024180 and 2024181. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0sc04596a



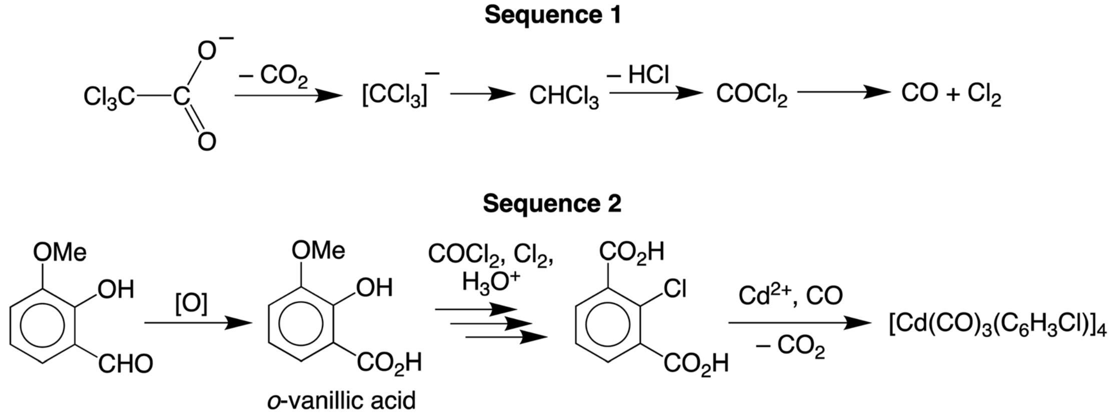
Scheme 1

afford 2-chlorobenzene-1,3-dicarboxylic acid upon hydrolysis, and (iii) decarboxylation of the 2-chlorobenzene-1,3-dicarboxylic acid to generate the $(C_6H_3Cl)^{2-}$ dianion which, in the presence of Cd^{2+} and CO, forms $[Cd(CO)_3(C_6H_3Cl)]_4$.

The carbonyl compound $[Cd(CO)_3(C_6H_3Cl)]_4$ attracted our attention because, if it were to be extended to zinc, the system could provide novel chemistry relevant to catalysis involving CO. However, prior to embarking on such a study, we considered it pertinent to evaluate the nature of $[Cd(CO)_3(C_6H_3Cl)]_4$ in more detail. Since the structural characterization of $[Cd(CO)_3(C_6H_3Cl)]_4$ relied on single crystal X-ray diffraction, which is a technique that may be subject to misinterpretation,[20,21] we retrieved the data for $[Cd(CO)_3(C_6H_3Cl)]_4$ that were deposited in the Cambridge Structural Database (CSD)[22] for further investigation.

Atom displacement parameters are an important aspect of assessing the correctness of atom assignments, and so we evaluated the parameters both visually *via* an atom displacement plot (Fig. 1) and quantitatively in terms of their absolute and relative values (Table 1). Examination of the atom displacement plot (Fig. 1) indicates that the displacement parameters for the cadmium atoms are exceptionally small by comparison to the other atoms; alternatively, the displacement parameters for the outer atoms are much larger than those for cadmium. For example, the average U_{eq} value for the cadmium atoms is 0.020 Å^2, while those for the carbonyl carbon, carbonyl oxygen and ring carbon atoms are 0.098 Å^2, 0.122 Å^2 and 0.074 Å^2, respectively. If normalized to a value of 1.00 Å^2 for cadmium, these correspond to values of 4.96 Å^2, 6.19 Å^2 and 3.73 Å^2, respectively. Although it is not unusual for the central atom in a molecule to have smaller displacement parameters than the outer atoms, the magnitude of the difference is not usually this large.

As an illustration, the displacement parameters for some binary carbonyl compounds are summarized in Table 1.[23–26] Thus, relative to a value of 1.00 Å^2 for U_{eq} of the metal atom, the carbonyl carbon atoms of the binary carbonyl compounds range from 1.41 Å^2 to 1.53 Å^2, while the values for the oxygen atoms range from 2.16 Å^2 to 2.46 Å^2. The very large relative values of 4.96 Å^2 and 6.19 Å^2 for the carbon and oxygen atoms of the carbonyl ligands of $[Cd(CO)_3(C_6H_3Cl)]_4$, therefore, clearly indicate that the relative U_{eq} values for the cadmium atoms of $[Cd(CO)_3(C_6H_3Cl)]_4$ are anomalously small; it must be emphasized, however, that it is the relative



Scheme 2

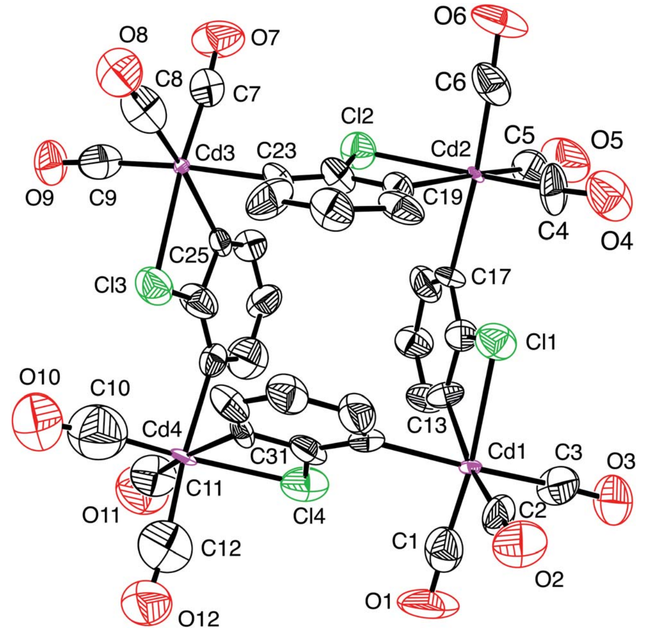


Fig. 1 Atom displacement plot for $[Cd(CO)_3(C_6H_3Cl)]_4$ with data taken from CCDC #185365 (40% displacement parameters).

value of U_{eq} for Cd that is anomalous, because the absolute value is not exceptionally unusual. For example, the value of U_{eq} for Cd (0.020 Å^2) is within the range (0.009 Å^2 to 0.029 Å^2) reported for the metals in the binary carbonyl compounds (Table 1).

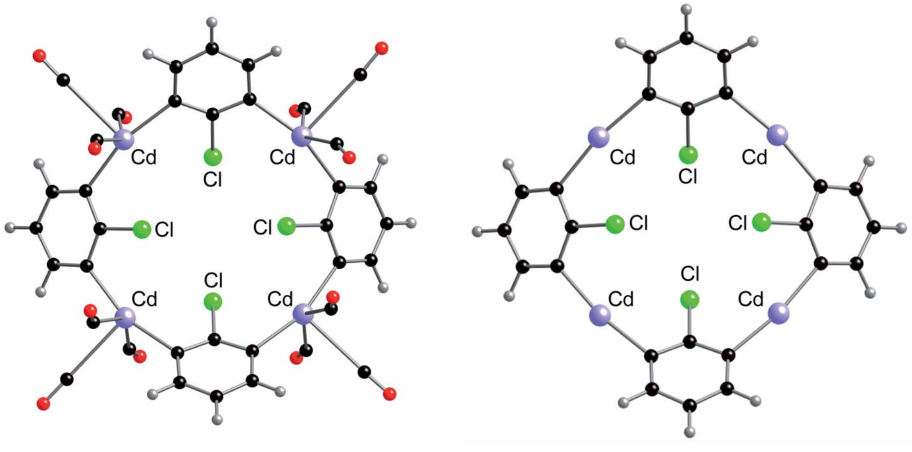
The unusually small displacement parameters for the cadmium atoms relative to the other atoms in $[Cd(CO)_3(C_6H_3Cl)]_4$ strongly indicate that the cadmium atoms have been misidentified and should be reassigned to a heavier atom.[27] Support for the proposal that the metal atoms are not cadmium is provided by the fact that the density functional theory (DFT) geometry optimized structure of $[Cd(CO)_3(C_6H_3Cl)]_4$ (Fig. 2), using the coordinates of the experimental structure, failed to converge to a similar structure to that reported (Fig. 1).[4]

Key differences between the geometry optimized structure (Fig. 2, left) and that derived by X-ray diffraction (Fig. 1) are summarized in Table 2. Specifically: (i) the C_{Ar}–Cd–C_{Ar} bond angles in the experimentally reported structure of $[Cd(CO)_3(C_6H_3Cl)]_4$ are very bent (84.4°), whereas the geometry optimized values are almost linear (162.2°); (ii) the Cd–Cl distances in the experimentally reported structure of $[Cd(CO)_3(C_6H_3Cl)]_4$ are asymmetric (2.53 Å and 3.68 Å), with there being a much closer interaction between each chlorine and one of the cadmium atoms, whereas each chlorine in the geometry optimized structure is located symmetrically between two Cd centers, with distances (3.19 Å and 3.21 Å) that are beyond normal bonding interactions; (iii) the three carbonyl ligands possess a *fac* disposition in the experimental structure (C_{CO}–Cd–C_{CO} bond angles in the range 86.4°–88.9°) but a *mer* disposition in the geometry optimized structure (C_{CO}–Cd–C_{CO}

Table 1 Average values for equivalent isotropic displacement parameters (Å^2) for some metal carbonyl compounds[a]

	$U_{eq}(M)$	$U_{eq}(C)$	$U_{eq}(O)$	$U_{eq}(M)_{rel}$	$U_{eq}(C)_{rel}$	$U_{eq}(O)_{rel}$	Ref.
$Cr(CO)_6$	0.009	0.014	0.020	1.00	1.45	2.20	23
$Mo(CO)_6$	0.018	0.025	0.041	1.00	1.41	2.28	24
$W(CO)_6$	0.029	0.041	0.067	1.00	1.42	2.34	25
$Fe(CO)_5$	0.014	0.022	0.035	1.00	1.53	2.46	26
$Ni(CO)_4$	0.016	0.023	0.035	1.00	1.41	2.16	26
$[Cd(CO)_3(C_6H_3Cl)]_4$	0.020	0.098	0.122	1.00	4.96	6.19	4

[a] $U_{eq}(X)_{rel} = U_{eq}(X)/U_{eq}(M)$



$[Cd(CO)_3(C_6H_3Cl)]_4$ $[Cd(C_6H_3Cl)]_4$

Fig. 2 DFT geometry optimized structure of $[Cd(CO)_3(C_6H_3Cl)]_4$ (left) and $[Cd(C_6H_3Cl)]_4$ (right).

Table 2 Comparison of average metrical data for each Cd center of the experimentally reported structure of $[Cd(CO)_3(C_6H_3Cl)]_4$ and the DFT geometry optimized structures of $[Cd(CO)_3(C_6H_3Cl)]_4$ and $[Cd(C_6H_3Cl)]_4$

	$[Cd(CO)_3(C_6H_3Cl)]_4$	$[Cd(CO)_3(C_6H_3Cl)]_4$	$[Cd(C_6H_3Cl)]_4$
	Experimental[a]	DFT	DFT
d(Cd–CO)/Å	1.855	2.901	—
d(Cd–C_{Ar})/Å	2.194	2.217	2.200
d(Cd–Cl_{short})/Å	2.526	3.187	3.113
d(Cd–Cl_{long})/Å	3.680	3.211	3.121
C_{Ar}–Cd–C_{Ar}/°	84.44	162.15	169.98
C_{CO}–Cd–C_{CO}/°	86.35	76.00	—
C_{CO}–Cd–C_{CO}/°	88.17	76.06	—
C_{CO}–Cd–C_{CO}/°	88.90	151.54	—
Cd–C–O/°	174.64	163.42	—

[a] Data taken from ref. 4.

bond angles of 76.0°, 76.1° and 151.5°); (iv) the Cd–C–O bond angles in the experimentally determined structure are close to linear (174.6°) but become much more bent in the geometry optimized structure (163.4°); and (v) finally, and most significantly, the average Cd–CO distance increases considerably from 1.86 Å in the experimental structure to 2.90 Å in the geometry optimized structure. The latter two observations indicate that Cd–CO interactions in $[Cd(CO)_3(C_6H_3Cl)]_4$ are not significant. Therefore, we also geometry optimized the counterpart with no carbonyl ligands, and, importantly, the structure of $[Cd(C_6H_3Cl)]_4$ is very similar to the same moiety in $[Cd(CO)_3(C_6H_3Cl)]_4$ (Fig. 2 and Table 2).

While both (i) the atom displacement parameters and (ii) the deviation of the geometry optimized structure from the experimentally determined structure clearly indicate that the identity of the metal atom needs to be reassigned, consideration should also be given to the possibility that the identities of other atoms may also need to be reevaluated, especially since it is well known[20,21] that atoms that have similar atomic numbers (*e.g.* B/C,[28,29] B/N,[30] C/N,[31] C/O,[32] N/O,[28,33,34] O/F,[35,36] Si/Cl[36] and Cl/S[37,38]) are often difficult to differentiate by X-ray diffraction.

In this regard, analysis of compounds listed in the CSD indicates that, other than $[Cd(CO)_3(C_6H_3Cl)]_4$, there are no structurally characterized compounds that feature a bridging C_6H_3Cl ligand. Moreover, there are only two examples of compounds that have a related C_6H_4Cl ligand coordinated to a single metal center, namely a zirconium compound[39] and an iridium compound.[40–42] Although the paucity of compounds with a κ^2-chloroaryl ligand is not a reason to exclude them from consideration, it does suggest that other possibilities should be considered. Since there are occurrences of Cl/S misidentification in the literature,[37,38] the possibility that the substituent on the aromatic ring is sulfur merits serious consideration, as does the possibility that the other atoms coordinated to cadmium are not carbon, but nitrogen. Indeed, analysis of the CSD indicates that six-membered heterocyclic nitrogen ligands with sulfur coordinated to a metal are common. Specifically, there are 255 structurally characterized examples of compounds with a κ^2-pyridine thiolate ligand,[43] and 134 examples of compounds with κ^2-pyridimine thiolate ligands.[44,45]

Assuming that the compound proposed to be "$[Cd(CO)_3(C_6H_3Cl)]_4$" is a carbonyl compound, chemical bonding considerations, as discussed earlier, dictate that the cadmium should be replaced with a transition metal. In this regard, while cadmium is located closer to the second than the third transition metal series, the fact that the displacement parameter is anomalously small relative to the other atoms requires that the new metal be selected from the third transition series. The most likely candidates are W, Re and Os, which are well known to form six-coordinate tricarbonyl compounds; of these, rhenium derivatives are the most common.[46] Recognizing that transition metal carbonyl compounds typically adopt 18-electron configurations, it is evident that, according to the covalent bond classification,[47] the purported "(C_6H_3Cl)" moiety must be reassigned to an L_3 donor for W, an L_2X donor for Re, and an LX_2 donor for Os. Focusing on the above heterocyclic nitrogen ligands derived from 2-mercaptopyridine and 2-mercaptopyrimidine, the possible bonding situations are illustrated in Fig. 3.

Of these possibilities, the L_2X coordination mode afforded by the pyrimidine thiolate ligand (Fig. 3) is appealing because it is evident that potential compounds can be straightforwardly obtained from commercially available 2-

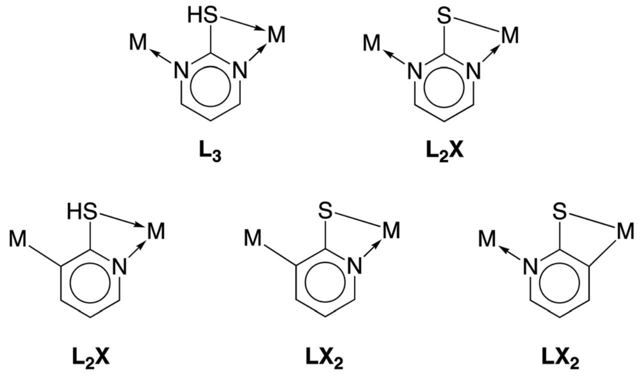
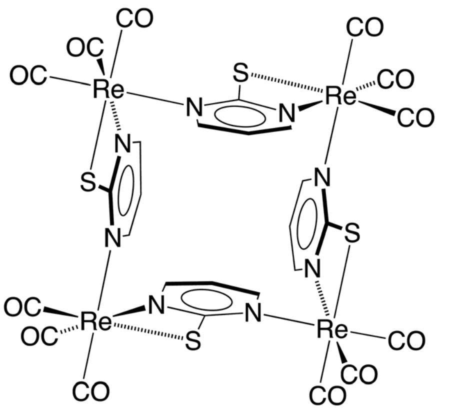


Fig. 3 Covalent bond classification of potential bridging ligands derived from 2-mercaptopyrimidine (top) and 2-mercaptopyridine (bottom).



$[Re(CO)_3(C_4N_2H_3S)]_4$

Fig. 4 A tetranuclear rhenium tricarbonyl pyrimidine-2-thiolate compound.

mercaptopyrimidine.[44,48] Indeed, pyrimidine-2-thiolate compounds are well known and the rhenium compound $[Re(CO)_3(C_4N_2H_3S)]_4$ (Fig. 4) has been reported.[44a] The critical issue, however, is whether the X-ray diffraction data for $[Re(CO)_3(C_4N_2H_3S)]_4$ could reproduce the structure reported for $[Cd(CO)_3(C_6H_3Cl)]_4$, not only in terms of metrical details and atom displacement parameters, but also in terms of providing reasonable refinement parameters such that the results could be considered publishable. In view of the fact that cadmium ($Z = 48$) and rhenium ($Z = 75$) differ by the substantial value of 27 in terms of their atomic numbers, such that they have very different X-ray scattering powers, it is not at all obvious that it is possible to misassign these elements and yet still achieve a publishable structure. To provide an answer to this issue, it is necessary to refine a dataset for $[Re(CO)_3(C_4N_2H_3S)]_4$ as the cadmium compound, $[Cd(CO)_3(C_6H_3Cl)]_4$. While the positional parameters of the former are available,[44a] the required structure factors have not been reported,[49] and so we collected X-ray diffraction data on $[Re(CO)_3(C_4N_2H_3S)]_4$.

As is evident from Fig. 5, the molecular structure of $[Re(CO)_3(C_4N_2H_3S)]_4$ shows a striking resemblance to that for $[Cd(CO)_3(C_6H_3Cl)]_4$ (Fig. 1).[4] The crystallographic data for $[Re(CO)_3(C_4N_2H_3S)]_4$ were, therefore, subsequently refined as $[Cd(CO)_3(C_6H_3Cl)]_4$ (Fig. 6), which hereafter will be referred to as "$[Cd(CO)_3(C_6H_3Cl)]_4$-**Re**" to indicate that the cadmium structure is based on the rhenium data set. Significantly, there is excellent agreement between the respective bond lengths of $[Cd(CO)_3(C_6H_3Cl)]_4$-**Re** and the published structure of $[Cd(CO)_3(C_6H_3Cl)]_4$, as illustrated in Fig. 7, with the average deviation in all bond lengths being only 0.039 Å. In addition to similar bond lengths, the relative atom displacement parameters of the two structures are also comparable (Table 3). The body of evidence, therefore, indicates that the reported structure of the novel cadmium carbonyl compound, $[Cd(CO)_3(C_6H_3Cl)]_4$, is actually that of the rhenium compound, $[Re(CO)_3(C_4N_2H_3S)]_4$.

The fact that the X-ray diffraction data for a rhenium compound can be interpreted as a cadmium compound is most consequential because this would not at all be expected due to the significantly different scattering powers of these elements. As such, it merits further discussion, and one factor that needs to be considered is the *R* value,[50] since this is typically used as a criterion to evaluate the reliability of a structure determination. In this regard, while the *R* value for the cadmium refinement (6.78%) is, as would be expected, higher than that for the rhenium refinement (3.43%), it is certainly acceptable for publication since structures with much higher *R* values appear

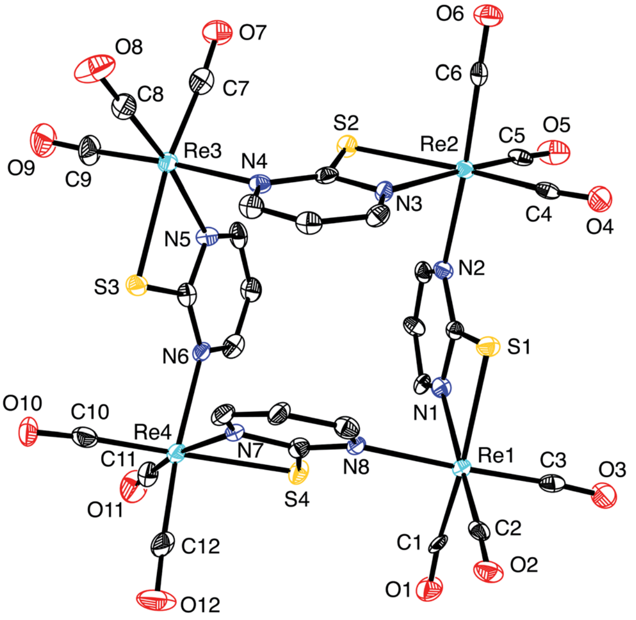


Fig. 5 Atom displacement plot for $[Re(CO)_3(C_4N_2H_3S)]_4$ (40% displacement parameters).

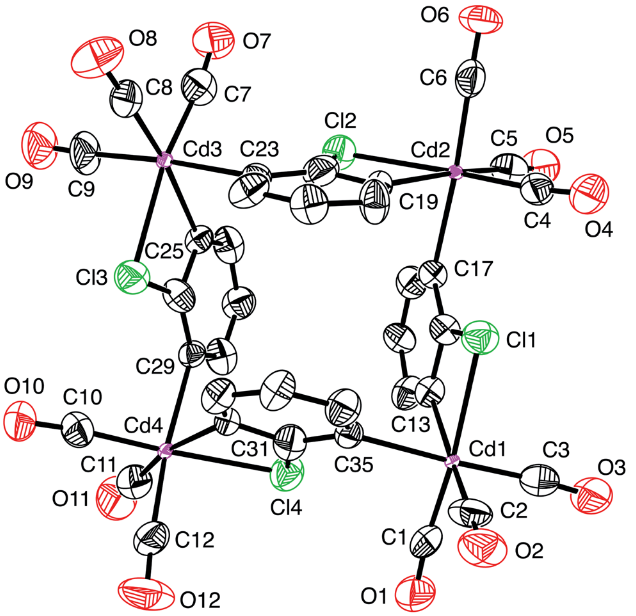


Fig. 6 Atom displacement plot for $[Cd(CO)_3(C_6H_3Cl)]_4$-**Re** using experimental data for $[Re(CO)_3(C_4N_2H_3S)]_4$ (40% displacement parameters).

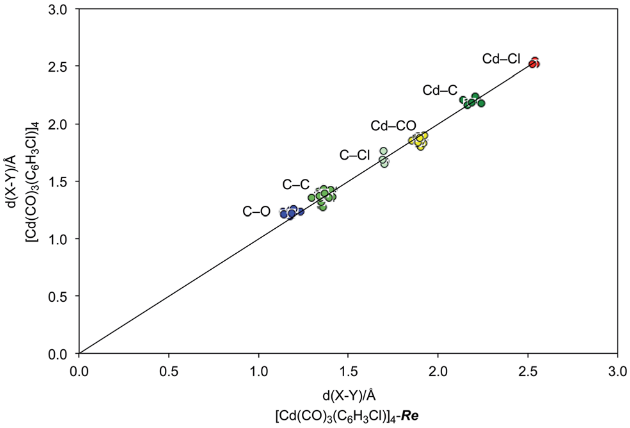


Fig. 7 Comparison of the bond lengths of $[Re(CO)_3(C_4N_2H_3S)]_4$, refined as $[Cd(CO)_3(C_6H_3Cl)]_4$-**Re**, with those of the published data for $[Cd(CO)_3(C_6H_3Cl)]_4$,[4] demonstrating an excellent correspondence.

Table 3 Relative average U_{eq} values[a] for $[Re(CO)_3(C_4N_2H_3S)]_4$, refined as $[Cd(CO)_3(C_6H_3Cl)]_4$-**Re**, together with those of the published data for $[Cd(CO)_3(C_6H_3Cl)]_4$

	$[Cd(CO)_3(C_6H_3Cl)]_4$-**Re**	$[Cd(CO)_3(C_6H_3Cl)]_4$[b]
$U_{eq}(Cd)_{rel}$	1	1
$U_{eq}(C_{CO})_{rel}$	4.80	4.96
$U_{eq}(O)_{rel}$	6.43	6.19
$U_{eq}(Cl)_{rel}$	4.47	3.87
$U_{eq}(C_{CdC})_{rel}$	2.89	2.29
$U_{eq}(C_{ring})_{rel}$	4.25	3.73

[a] $U_{eq}(X)_{rel} = U_{eq}(X)/U_{eq}(Cd)$. [b] Data taken from ref. 4.

commonly in the chemistry literature. For example, of the structurally characterized cadmium compounds listed in the CSD, 20.4% have *R* values greater than 6.00%.[51] In fact, the CSD contains structures of cadmium compounds with *R* values as high as 30.1%.[52] Thus, the *R* value for $[Cd(CO)_3(C_6H_3Cl)]_4$-**Re** cannot be used in the present case as a definitive gauge of an incorrect structure.

Although the *R* value for $[Cd(CO)_3(C_6H_3Cl)]_4$-**Re** does not necessarily indicate an incorrect structure, the small value of U_{eq} for cadmium relative to the other atoms does indicate that there is a problem. To illustrate in more detail the impact of the incorrect atom assignment on the derived displacement parameters, the U_{eq} data for $[Re(CO)_3(C_4N_2H_3S)]_4$ and its refinement as the cadmium complex, $[Cd(CO)_3(C_6H_3Cl)]_4$-**Re**, are compared in Table 4 and Fig. 8. These data indicate that not only is U_{eq} for the cadmium smaller than the value for rhenium in the correct refinement, but the values for the other atoms are all significantly larger, as indicated by the fact that they lie above the correlation line with a slope of unity (Fig. 8). More specifically, whereas $U_{eq}(Cd)/U_{eq}(Re)$ is 0.71, the average ratios for the other groups of atoms are in the range 2.10–2.75 (Table 4).

Examination of the trendline through the atoms that have the same assignments in both refinements (*i.e.* the carbonyl groups and ring carbon atoms) illustrates that there is a distinct shift of the nitrogen atoms that are incorrectly refined as carbon atoms (Fig. 8). This anomaly is of note because even close visual inspection of the atom displacement plots (Fig. 6) does not signal an obvious error in the assignment of the N/C pairs of atoms.

Table 4 Average U_{eq} values for $[Re(CO)_3(C_4N_2H_3S)]_4$ and the structure refined as $[Cd(CO)_3(C_6H_3Cl)]_4$-**Re**

X	$[Re(CO)_3(C_4N_2H_3S)]_4$	$[Cd(CO)_3(C_6H_3Cl)]_4$-**Re**	$U_{eq}(X)_{rel}$[a]
M	0.021	0.015	0.71
S/Cl	0.024	0.066	2.75
C_{CO}	0.029	0.070	2.41
O	0.044	0.094	2.14
N/C	0.020	0.042	2.10
C_{ring}	0.023	0.062	2.70

[a] $U_{eq}(X)_{rel} = U_{eq}(X)[Cd(CO)_3(C_6H_3Cl)]_4\text{-}\mathbf{Re}/U_{eq}(X)[Re(CO)_3(C_4N_2H_3S)]_4$.

In contrast to the shift observed for the N/C pairs of atoms (Fig. 8), the S/Cl pairs are not discernably displaced from the trendline because the proportional difference in atomic numbers[53] between S and Cl (6.25%) is less than that between N and C (16.67%). Therefore, it is not surprising that visual inspection of the atom displacement plots (Fig. 6) likewise provides no clear indication that the chlorine atoms are misassigned. In many cases, incorrect atom assignments are indicated by the observation of unusual "cigar" or "disk" shaped ellipsoids or by refinements that result in atoms becoming "non-positive definite".[21a–d] However, in the present case, the incorrect atom assignments result in none of the atoms either becoming "non-positive definite" or exhibiting particularly unusual shapes. Instead, the assignment of rhenium as cadmium causes the U_{eq} values for all other atoms to increase in

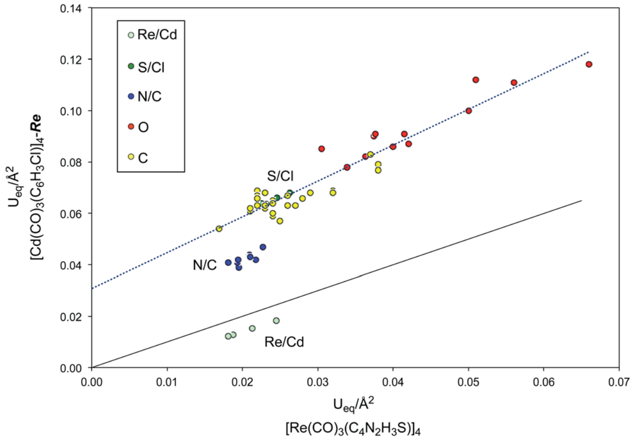


Fig. 8 Comparison of U_{eq} values for $[Re(CO)_3(C_4N_2H_3S)]_4$ and the structure refined as the cadmium compound, $[Cd(CO)_3(C_6H_3Cl)]_4$-**Re**. The solid line has a slope of unity and depicts the boundary that indicates whether the U_{eq} values for the incorrectly refined structure are larger or smaller than the correct structure. The dashed line is drawn through all atoms that have the same assignments in both structures. Note that the misidentified Re/Cd and N/C pairs are in distinct locations, in contrast to the S/Cl pairs which cannot be distinguished on this basis.

an approximately uniform manner, such that if one were to focus on the nonmetal atoms, the structure could appear to be normal. Indeed, the enlarged atom displacement parameters could also have been interpreted in terms of thermal motion.

In addition to the discrepancy in the magnitudes of the atom displacement parameters, another indication that there is a problem with atom assignments may be obtained by evaluating the results of a Hirshfeld "rigid-bond" analysis.[54–56] Specifically, since vibrations involving bond stretching are of higher energy than those involved in other vibrational modes, the components of the displacement parameters of two bonded atoms should be of similar magnitude along the direction of the bond. Thus, for two atoms (A and B), where $z_A{}^2$ and $z_B{}^2$ are the mean-square amplitudes along the bond, the difference $\Delta_{AB} = z_A{}^2 - z_B{}^2$ is expected to be approximately zero.[54,55] Indeed, the C–C, C–N and C–O bonds in organic compounds are typically characterized by values of Δ_{AB} less than 0.001 Å^2.[54,55] However, for metal compounds, in which there is a large difference in mass between the metal and the coordinating atom, values of Δ_{AB} of approximately 0.003 Å^2 (*i.e.* $\sqrt{\Delta_{AB}} \approx 0.05$ Å) are typical (with the lighter atom having the larger value of z^2),[57] although much larger values of Δ_{AB} have been reported for metal carbonyl compounds, *e.g.* 0.0148 Å^2 (*i.e.* $\sqrt{\Delta_{AB}} \approx 0.12$ Å) for $[(PPh_3)RuCo(CO)_6(\mu\text{-}PPh_2)]$.[58] In this regard, application of the Hirshfeld analysis to $[Cd(CO)_3(C_6H_3Cl)]_4$-**Re** indicates that the $\sqrt{\Delta_{AB}}$ values for the Cd–X bonds of $[Cd(CO)_3(C_6H_3Cl)]_4$-**Re** are particularly large and range from 0.14 Å to 0.26 Å, with an average value of 0.21 Å.[59,60] As such, it is clear that this test provides further evidence that the cadmium center of $[Cd(CO)_3(C_6H_3Cl)]_4$-**Re** is misassigned.

Since the displacement parameters do indeed provide evidence for the atom misassignment, some consideration needs to be given as to why it went unnoticed. With respect to this issue, it appears that the structural determination of coordination compounds often seems to focus on the atoms associated with the ligands, rather than the central metal, a bias that is presumably a consequence of the belief that the metal is not usually in doubt. However, there are certainly rational means by which a compound analyzed may not contain the presumed metal, which include (i) accidentally selecting an incorrect container of a reagent for the synthesis of the compound, (ii) unnoticed metal contamination resulting from an earlier step in the reaction sequence, and (iii) accidentally selecting the incorrect vial of crystals while preparing the sample for data collection.[61] If possibilities such as these are not considered, it is understandable how, without careful scrutiny, the true identity of the central atom may go unrecognized. The present example serves as a reminder that exceptional care is often required to verify the identity of a compound, which is especially necessary when the proposed structure is novel;[62,63] furthermore, in addition to spectroscopic and analytical data, a computational analysis of the proposed structure could also be used to provide useful corroborating data.

Single crystal X-ray diffraction plays a critical role in the chemical sciences,[64,65] such that it is important to appreciate how misinterpretations may occur. The present example is of particular note because the ability to refine successfully a compound that contains rhenium as one that contains cadmium, two metals that differ substantially in their atomic numbers ($\Delta Z = 27$), is unexpected. Other reports of misidentification in ordered structures typically involve atoms that possess similar atomic numbers,[66–69] and so the example described here indicates that the problem may be more widespread than realized; it also emphasizes the importance of paying close attention to the displacement parameters of all atoms when evaluating a structure refinement model.

Summary

In conclusion, the structure reported for the cadmium carbonyl compound $[Cd(CO)_3(C_6H_3Cl)]_4$, with bridging chloroaryl ligands, is actually that of the rhenium compound $[Re(CO)_3(C_4N_2H_3S)]_4$, with bridging pyrimidine-2-thiolate ligands. As such, three pairs of atoms, namely Re/Cd, S/Cl and N/C, have been misidentified. Of these, the misidentification involving Re and Cd is most consequential because of the significant disparity in their X-ray scattering powers due to their large difference in atomic numbers ($\Delta Z = 27$). Thus, while it is well known that X-ray diffraction may not reliably distinguish between atoms with similar atomic number (*e.g.* C and N), the ability of pairs of atoms with very different atomic numbers to be misidentified is not well appreciated. The ability to refine $[Re(CO)_3(C_4N_2H_3S)]_4$ as $[Cd(CO)_3(C_6H_3Cl)]_4$, with an *R* value that is of publication quality, is remarkable and serves as a caveat, especially when reporting the structures of novel compounds.

Experimental section

X-ray structure determination

Crystals of previously reported $[Re(CO)_3(C_4N_2H_3S)]_4$[44a] suitable for X-ray diffraction were obtained from CH_2Cl_2.[70] X-ray diffraction data were collected on a Bruker Apex II diffractometer, and the structure was solved by using direct methods and standard difference map techniques, and was refined by full-matrix least-squares procedures on F^2 with SHELXTL (version 2014/7).[71] The asymmetric unit contains two molecules of CH_2Cl_2, one of which is disordered over two positions and was modeled by using SADI and EADP restraints. The structure was also refined as $[Cd(CO)_3(C_6H_3Cl)]_4$ to illustrate the impact of incorrect atom assignments on the atom displacement parameters and refinement parameters. The Hirshfeld test was performed with PLATON.[56a,b,72] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 2024180-2024181).

Computational details

Calculations were carried out using DFT as implemented in the Jaguar 8.9 (release 15) suite of *ab initio* quantum chemistry programs.[73] Geometry optimizations were performed with the B3LYP density functional using the LACVP** basis sets and Cartesian coordinates are provided in the ESI.†

Conflicts of interest

There are no conflicts to declare.

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46 For example, the distribution in the number of metal tricarbonyl compounds for the third transition series metals is: Sc (0), Hf (1), Ta (6), W (2,754), Re (4,339), Os (2,207), Ir (157) and Pt (0). See ref. 22.

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48 In this regard, it is worth noting that there are no structurally characterized examples of the L_2X and LX_2 motifs derived from 2-mercaptopyridine, or L_3 motifs derived from 2-mercaptopyrimidine.

49 Likewise, the structure factors for $[Cd(CO)_3(C_6H_3Cl)]_4$ are not published.

50 R refers to the conventional discrepancy index of $R1 = [\Sigma||F_o| - |F_c||]/[\Sigma|F_o|]$ for $I > 2\sigma(I)$.

51 These percentages are for compounds for which the R value is listed.

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57 (*a*) J. D. Dunitz, E. F. Maverick and K. N. Trueblood, Atomic motions in molecular crystals from diffraction measurements, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 880–895; (*b*) J. D. Dunitz, V. Schomaker and K. N. Trueblood, Intrepretation of atomic displacement parameters from diffraction studies of crystals, *J. Phys. Chem.*, 1988, **92**, 856–867.

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59 The other X–Y bonds in the molecule have $\sqrt{\varDelta_{AB}}$ values that range from 0.03 Å to 0.23 Å, with an average value of 0.12 Å.

60 In addition to the absolute magnitude of $\varDelta_{AB}$, the ratio of $\varDelta_{AB}$ to its standard uncertainty (σ) has also been considered as an indicator of incorrect atom assignment (ref. 53) and, in this regard, many Cd–X bonds fail at the 5σ level: Cd1–C1 (5.15), Cd1–C3 (5.23), Cd2–C6 (5.23), Cd3–Cl3 (14.67), Cd4-Cl4 (15.67), Cd2–Cl2 (16.00) and Cd1–Cl1 (16.33).

61 In this regard, an author of ref. 4 has published structures of a variety of rhenium compounds. See, for example: (*a*) A. J. Amoroso, A. Banu, M. P. Coogan, P. G. Edwards, G. Hossain and K. M. A. Malik, Functionalisation of terpyridine complexes containing the $Re(CO)_3^+$ moiety, *Dalton Trans.*, 2010, **39**, 6993–7003; (*b*) S. Dinda, D. K. Hazra, S. RoyChowdhury, M. Helliwell, K. M. A. Malik, M. Mukherjee and R. Bhattacharyya, Reductive thiocyanolysis of tetraoxorhenate (VII): Synthesis, crystal structure, catalytic oxidation and kinetic studies of $(PPh_4)_2[Re(NCS)_6]$ and $(PPh_4)_2[ReO(NCS)_5]$, *Inorg. Chim. Acta*, 2009, **362**, 2108–2116; (*c*) M. L. Creber, K. G. Orrell, A. G. Osborne, V. Šik, M. B. Hursthouse and K. M. A. Malik, Dynamic NMR investigations of fluxionality of 2-(dimethoxymethyl)pyridine and 2,6-bis(dimethoxymethyl)pyridine in rhenium(I) and platinum(IV) complexes, *J. Chem. Soc., Dalton Trans.*, 2000, 4218–4226; (*d*) R. J. Baker, P. G. Edwards, J. Garcia-Mora, F. Ingold and K. M. A. Malik, Manganese and rhenium triphosphorus macrocycle complexes and reactions with alkenes, *J. Chem. Soc., Dalton Trans.*, 2002, 3985–3992; (*e*) A. Gelling, K. G. Orrell, A. G. Osborne, V. Šik, M. B. Hursthouse, D. E. Hibbs and K. M. A. Malik, Synthesis and dynamic NMR studies of Rhenium(I) tricarbonyl bromide complexes of benzimidazolylpyridine ligands. Crystal structure of $[ReBr(CO)_3\{$2,6-bis(1',5',6'-trimethylbenzimidazol-2'-yl)pyridine$\}]$, *Polyhedron*, 1998, **17**, 2141–2151; (*f*) K. A. Azam, M. A. Hossain, M. B. Hursthouse, S. E. Kabir, K. M. A. Malik and H. Vahrenkamp, Photochemical reaction of $Re_2(CO)_{10}$ with tetramethylthiourea; structural characterization of two novel pentarhenium carbonyl complexes containing sulfido and tetramethyldiaminocarbene ligands, $[Re_5(CO)_{17}(\mu\text{-}R)(\mu_4\text{-}S)_2\{C(NMe_2)_2\}_2]$ (R = SH or OH), *J. Organomet. Chem.*, 1998, **555**, 285–292; (*g*) K. G. Orrell, A. G. Osborne, V. Šik, M. W. da Silva, M. B. Hursthouse, D. E. Hibbs, K. M. A. Malik and N. G. Vassilev, Stereochemically non-rigid transition metal complexes of 2,6-bis[(1-phenylimino)ethyl]pyridine (BIP) Part 2. Dynamic NMR studies of *fac*-$[ReX(CO)_3(BIP)]$ (X = Cl, Br, or I). Crystal structure of *fac*-$[ReBr(CO)_3(BIP)]$, *J. Organomet. Chem.*, 1997, **538**, 171–183; (*h*) M. T. Ahmet, C. Lu, J. R. Dilworth, J. R. Miller, Y. Zheng, D. E. Hibbs, M. B. Hursthouse and K. M. A. Malik, Synthesis of complexes of Re^{V}, Ru^{II}, Os^{II}, Rh^{I}, Ir^{I} and Ir^{III}. Crystal and molecular structures of $[ReO(OH)(SC_6H_4SiPh_3\text{-}2)_2(PPh_3)]$, $[ReH_4(SC_6H_4SiPh_3\text{-}2)(PPh_3)_3]$ and $[IrH(SC_6H_4SiPh_3\text{-}2)_2(PMePh_2)_3]$, *J. Chem. Soc., Dalton Trans.*, 1995, 3143–3152; (*i*) M. T. Ahmet, B. Coutinho, J. R. Dilworth, J. R. Miller, S. J. Parrott, Y. Zheng, M. Harman, M. B. Hursthouse and A. Malik, Synthesis and characterization of organoimido- and organoamido-rhenium(V) complexes. Crystal structures of $[ReCl_2(NC_6H_4PPh_2\text{-}2)(HNC_6H_4PPh_2\text{-}2)]$, $[Re(8\text{-}HNC_9H_6N)_2O(PPh_3)][BPh_4]$ and $[Re(NPh)(NC_5H_3S\text{-}2\text{-}SiMe_3\text{-}3)_2(PPh_3)][BPh_4]$, *J. Chem. Soc., Dalton Trans.*, 1995, 3041–3048.

62 As an illustration, the ^{13}C NMR spectroscopic signals of the carbonyl groups of $[Cd(CO)_3(C_6H_3Cl)]_4$ would be expected to exhibit cadmium satellites (^{111}Cd, 12.80%; ^{113}Cd,12.22%) that would provide excellent evidence for a Cd–CO moiety, but none were reported; also, chlorine elemental analysis would have provided convincing evidence for the chloroaryl ligand, but was not listed (ref. 4).

63 Co-crystallization of platinum, palladium and gold polyoxometallates with the tungsten derivative has also resulted in the misidentification of compounds. See: K. P. O'Halloran, C. C. Zhao, N. S. Ando, A. J. Schultz, T. F. Koetzle, P. M. B. Piccoli, B. Hedman, K. O. Hodgson, E. Bobyr, M. L. Kirk, S. Knottenbelt, E. C. Depperman, B. Stein, T. M. Anderson, R. Cao, Y. V. Geletii, K. I. Hardcastle, D. G. Musaev, W. A. Neiwert, X. K. Fang, K. Morokuma, S. X. Wu, P. Kogerler and C. L. Hill, Revisiting the polyoxometalate-based late-transition-metal-oxo complexes: The 'oxo wall' stands, *Inorg. Chem.*, 2012, **51**, 7025–7031.

64 S. J. Coles and P. A. Gale, Changing and challenging times for service crystallography, *Chem. Sci.*, 2012, **3**, 683–689.

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66 In addition to the aforementioned instances of misidentification involving nonmetals,[28–38] other examples include Cu being incorrectly refined as Co,[a-c] Br being incorrectly refined as Cu,[d,e] O being incorrectly refined as S,[f,g] Br being incorrectly refined as Ag,[d,e] Zn being incorrectly refined as Mo,[h,i] Sn being incorrectly refined as Se;[j,k,l] Ni (or possibly Co or Zn) being incorrectly refined as Pd,[m,n] and a combination of Ni/Cl/N being incorrectly refined as Ln/Ni/Cl (Ln = Eu, Ce, Gd).[o,p] (*a*) V. D. Vreshch, J. H. Yang, H. T. Zhang, A. S. Filatov and E. V. Dikarev, Monomeric square-planar cobalt(II) acetylacetonate: mystery or mistake?, *Inorg. Chem.*, 2010, **49**, 8430–8434; (*b*) J. Burgess, J. Fawcett and D. R. Russell, Bis(2,4-pentanedionato)cobalt(II), *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2011, **67**, e13; (*c*) F. A. Cotton and R. H. Holm, Magnetic investigations of spin-free cobaltous complexes. III. On the existence of planar complexes, *J. Am. Chem. Soc.*, 1960, **82**, 2979–2983; (*d*) A. Haaland, K. Rypdal, H. P. Verne, W. Scherer and W. R. Thiel, The crystal-structures of base-free, monomeric arylcopper(I) and arylsilver(I) compounds; 2 cases of mistaken identity?, *Angew. Chem., Int. Ed.*, 1994, **33**, 2443–2445; (*e*) R. Lingnau and J. Strähle, 2,4,6-$Ph_3C_6H_2M$ (M = Cu, Ag), monomeric Cu^{I}-complexes and Ag^{I}-complexes with coordination number 1, *Angew. Chem., Int. Ed.*, 1988, **27**, 436; (*f*) A. Ienco, M. Caporali, F. Zanobini and C. Mealli, Is 2.07 Å a record for the shortest Pt-S distance? Revision of two reported X-ray structures, *Inorg. Chem.*, 2009, **48**, 3840–3847; (*g*) H. Li, G. B. Carpenter and D. A. Sweigart, Models for homogeneous deep hydrodesulfurization. Intramolecular CO substitution by the sulfur in $[(\eta^6\text{-2-methylbenzothiophene})Mn(CO)_3]^+$ and $[(\eta^6\text{-dibenzothiophene})Mn(CO)_3]^+$ after regiospecific insertion of platinum into a C-S bond, *Organometallics*, 2000, **19**, 1823–1825; (*h*) F. A. Cotton and G. Schmid, Proposed reformulation of recently reported 'tetrahedral molybdenum(II)' complexes: Trimethylphosphine complexes of zinc chloride, *Polyhedron*, 1996, **15**, 4053–4059; (*i*) K. Fromm, M. Plaikner and E. Hey-Hawkins, Synthesis and molecular structures of the molybdenum(II) complexes $MoCl_2(PMe_3)_2$ and $[Mo(\mu\text{-}PPh_2)(PPh_2)(PMe_3)]_2$, *Z. Naturforsch., B: J. Chem. Sci.*, 1995, **50**, 894–898; (*j*) E. Rufino-Felipe, E. Osorio, G. Merino and M. A. Munoz-Hernandez, Do planar tetracoordinate tin complexes really exist?, *Dalton Trans.*, 2013, **42**, 11180–11185; (*k*) R. Cea-Olivares, J. Novosad, J. D. Woollins, A. M. Z. Slawin, V. Garcia-Montalvo, G. Espinosa-Perez and P. G. Y. Garcia, A true square-planar tin(II) spiro complex: Molecular structure of bis(imidotetraphenyldiselenodiphosphino-*Se*,*Se'*)tin(II) and its distorted tetragonal-pyramidal isomer, *Chem. Commun.*, 1996, 519–520; (*l*) R. Cea-Olivares, M. Moya-Cabrera, V. Garcia-Montalvo, R. Castro-Blanco, R. A. Toscano and S. Hernandez-Ortega, True square planar $[M\{N(SeP^iPr_2)_2\text{-}Se,Se'\}_2]$ [M = Sn, Se] complexes. An extraordinary geometrical arrangement for well known centers [Sn(II), Se(II)], *Dalton Trans.*, 2005, 1017–1018; (*m*) W. H. Zhang and T. S. A. Hor, Complexation of 1,1'-bis(diphenylphosphino)ferrocene dioxide ($dppfO_2$) with 3d metals and revisit of its coordination to Pd(II), *Dalton Trans.*, 2011, **40**, 10725–10730; (*n*) J. S. L. Yeo, J. J. Vittal and T. S. A. Hor, $PdCl_2(dppfO_2\text{-}O,O')$: a simple palladium(II) complex with a rare tetrahedral structure, *Chem. Commun.*, 1999, 1477–1478; (*o*) B. Baldo, F. Rubio, E. Flores, A. Vega, N. Audebrand, D. Venegas-Yazigi and V. Paredes-Garcia, $Ni_2[LnCl_6]$ (Ln = Eu^{II}, Ce^{II}, Gd^{II}): the first Ln^{II} compounds stabilized in a pure inorganic lattice, *Chem. Commun.*, 2018, **54**, 7531–7534; (*p*) B. Baldo, F. Rubio, E. Flores, A. Vega, N. Audebrand, D. Venegas-Yazigi and V. Paredes-Garcia, Retraction: $Ni_2[LnCl_6]$ (Ln = Eu^{II}, Ce^{II}, Gd^{II}): the first Ln^{II} compounds stabilized in a pure inorganic lattice, *Chem. Commun.*, 2019, **55**, 13183.

67 In this regard, it is pertinent to note that Donahue reported that a zinc compound had been refined as its Cr, Mo and W counterparts, but this was only possible by refining the heavy atom with partial occupancy such that it could artificially resemble the lighter zinc atom. See: (*a*) T. Turki, T. Guerfel and F. Bouachir, Synthesis, characterization and crystal structure of diamagnetic tetracoordinated chromium (II) complexes supported by α-diimine ligands, *Inorg. Chem. Commun.*, 2006, **9**, 1023–1025; (*b*) T. Turki, T. Guerfel and F. Bouachir, Synthesis and crystal structure of tetracoordinated molybdenum(II) complexes containing rigid α-diimine ligands, *Polyhedron*, 2006, **25**, 1142–1146; (*c*) T. Turki, T. Guerfel and F. Bouachir, Preparation and structural characterization of tetracoordinated tungsten(II) diazadiene complexes, *J. Organomet. Chem.*, 2006, **691**, 1857–1861; (*d*) A. F. Greene, P. Chandrasekaran, Y. Yan, J. T. Mague and J. P. Donahue, Element misidentification in X-ray crystallography: A reassessment of the $[MCl_2(\text{diazadiene})]$ (M = Cr, Mo, W) series, *Inorg. Chem.*, 2014, **53**, 308–317.

68 For an example of a disordered structure in which a half-occupancy Re site is refined as a full-occupancy Tc site, see: (*a*) A. K. Burrell, F. A. Cotton, L. M. Daniels and V. Petricek, Structure of crystalline $(C_5Me_5)ReO_3$ and implied nonexistence of "$(C_5Me_5)Tc_2O_3$", *Inorg. Chem.*, 1995, **34**, 4253–4255; (*b*) B. Kanellakopulos, B. Nuber, K. Raptis and M. L. Ziegler, A polymeric technetium compound of the composition $[Tc_2O_3(C_5Me_5)]_n$, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1055.

69 It should also be noted that, in addition to the accidental misidentification of elements, there are also deliberate examples that have resulted in many retractions. See, for example: (*a*) Editorial. W. T. A. Harrison, J. Simpson and M. Weil, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2010, **66**, e1–e2; (*b*) Retraction of articles by H. Zhong *et al.* H. Zhong, S. H. Duan, Y.-P. Hong, M.-L. Li, Y.-Q. Liu, C.-J. Luo, S.-Z. Xiao, H.-L. Xie, Y.-P. Xu, X.-M. Yang, X.-R. Zeng and Q. Y. Zhong, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2010, **66**, e11–e12; (*c*) Retraction of articles by T. Liu *et al.* T. Liu, Y.-X. Wang, Z.-W. Wang, Z.-P. Xie and J. Y. Zhu, *Acta Crystallogr., Sect. E: Struct. Rep.*

Online, 2010, **66**, e13–e14; (*d*) Retraction of articles, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2010, **66**, e21–e22; (*e*) Retraction of articles, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2011, **67**, e14.

70 In addition to the dichoromethane solvate reported here, $[Re(CO)_3(C_4N_2H_3S)]_4$ has also been crystallized as an ethanol solvate (ref. 44a) and as a hydrate when reported as $[Cd(CO)_3(C_6H_3Cl)]_4$ (ref. 4).

71 (*a*) G. M. Sheldrick, *SHELXTL, An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data*, University of Göttingen, Göttingen, Federal Republic of Germany, 1981; (*b*) G. M. Sheldrick, A short history of SHELX, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112–122; (*c*) G. M. Sheldrick, Crystal structure refinement with SHELXL, *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, **71**, 3–8.

72 https://www.platonsoft.nl/platon/.

73 (*a*) *Jaguar, version 8.9*, Schrodinger, Inc., New York, NY, 2015; (*b*) A. D. Bochevarov, E. Harder, T. F. Hughes, J. R. Greenwood, D. A. Braden, D. M. Philipp, D. Rinaldo, M. D. Halls, J. Zhang and R. A. Friesner, Jaguar: A high-performance quantum chemistry software program with strengths in life and materials sciences, *Int. J. Quantum Chem.*, 2013, **113**, 2110–2142.