

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<sub>6</sub>H<sub>3</sub>Cl)<sup>2-</sup> dianion which, in the presence of Cd<sup>2+</sup> and CO, forms [Cd(CO)<sub>3</sub>(C<sub>6</sub>H<sub>3</sub>Cl)]<sub>4</sub>.

The carbonyl compound [Cd(CO)<sub>3</sub>(C<sub>6</sub>H<sub>3</sub>Cl)]<sub>4</sub> 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)<sub>3</sub>(C<sub>6</sub>H<sub>3</sub>Cl)]<sub>4</sub> in more detail. Since the structural characterization of [Cd(CO)<sub>3</sub>(C<sub>6</sub>H<sub>3</sub>Cl)]<sub>4</sub> relied on single crystal X-ray diffraction, which is a technique that may be subject to misinterpretation,<sup>20,21</sup> we retrieved the data for [Cd(CO)<sub>3</sub>(C<sub>6</sub>H<sub>3</sub>Cl)]<sub>4</sub> that were deposited in the Cambridge Structural Database (CSD)<sup>22</sup> 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<sup>2</sup>, while those for the carbonyl carbon, carbonyl oxygen and ring carbon atoms are 0.098 Å<sup>2</sup>, 0.122 Å<sup>2</sup> and 0.074 Å<sup>2</sup>, respectively. If normalized to a value of 1.00 Å<sup>2</sup> for cadmium, these correspond to values of 4.96 Å<sup>2</sup>, 6.19 Å<sup>2</sup> and 3.73 Å<sup>2</sup>, 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.<sup>23–26</sup> Thus, relative to a value of 1.00 Å<sup>2</sup> for  $U_{eq}$  of the metal atom, the carbonyl carbon atoms of the binary carbonyl compounds range from 1.41 Å<sup>2</sup> to 1.53 Å<sup>2</sup>, while the values for the oxygen atoms range from 2.16 Å<sup>2</sup> to 2.46 Å<sup>2</sup>. The very large relative values of 4.96 Å<sup>2</sup> and 6.19 Å<sup>2</sup> for the carbon and oxygen atoms of the carbonyl ligands of [Cd(CO)<sub>3</sub>(C<sub>6</sub>H<sub>3</sub>Cl)]<sub>4</sub>, therefore, clearly indicate that the relative  $U_{eq}$  values for the cadmium atoms of [Cd(CO)<sub>3</sub>(C<sub>6</sub>H<sub>3</sub>Cl)]<sub>4</sub> are anomalously small; it must be emphasized, however, that it is the relative



Scheme 2





Fig. 1 Atom displacement plot for  $[\text{Cd}(\text{CO})_3(\text{C}_6\text{H}_3\text{Cl})]_4$  with data taken from CCDC #185365 (40% displacement parameters).

value of  $U_{\text{eq}}$  for Cd that is anomalous, because the absolute value is not exceptionally unusual. For example, the value of  $U_{\text{eq}}$  for Cd ( $0.020 \text{ \AA}^2$ ) is within the range ( $0.009 \text{ \AA}^2$  to  $0.029 \text{ \AA}^2$ )

Table 1 Average values for equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for some metal carbonyl compounds<sup>a</sup>

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

$$^a U_{\text{eq}}(\text{X})_{\text{rel}} = U_{\text{eq}}(\text{X})/U_{\text{eq}}(\text{M})$$



Fig. 2 DFT geometry optimized structure of  $[\text{Cd}(\text{CO})_3(\text{C}_6\text{H}_3\text{Cl})]_4$  (left) and  $[\text{Cd}(\text{C}_6\text{H}_3\text{Cl})]_4$  (right).

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  $[\text{Cd}(\text{CO})_3(\text{C}_6\text{H}_3\text{Cl})]_4$  strongly indicate that the cadmium atoms have been misidentified and should be reassigned to a heavier atom.<sup>27</sup> 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  $[\text{Cd}(\text{CO})_3(\text{C}_6\text{H}_3\text{Cl})]_4$  (Fig. 2), using the coordinates of the experimental structure, failed to converge to a similar structure to that reported (Fig. 1).<sup>4</sup>

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  $\text{C}_{\text{Ar}}-\text{Cd}-\text{C}_{\text{Ar}}$  bond angles in the experimentally reported structure of  $[\text{Cd}(\text{CO})_3(\text{C}_6\text{H}_3\text{Cl})]_4$  are very bent ( $84.4^\circ$ ), whereas the geometry optimized values are almost linear ( $162.2^\circ$ ); (ii) the Cd-Cl distances in the experimentally reported structure of  $[\text{Cd}(\text{CO})_3(\text{C}_6\text{H}_3\text{Cl})]_4$  are asymmetric ( $2.53 \text{ \AA}$  and  $3.68 \text{ \AA}$ ), 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 ( $3.19 \text{ \AA}$  and  $3.21 \text{ \AA}$ ) that are beyond normal bonding interactions; (iii) the three carbonyl ligands possess a *fac* disposition in the experimental structure ( $\text{C}_{\text{CO}}-\text{Cd}-\text{C}_{\text{CO}}$  bond angles in the range  $86.4^\circ$ – $88.9^\circ$ ) but a *mer* disposition in the geometry optimized structure ( $\text{C}_{\text{CO}}-\text{Cd}-\text{C}_{\text{CO}}$







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

mercaptopyrimidine.<sup>44,48</sup> Indeed, pyrimidine-2-thiolate compounds are well known and the rhenium compound  $[\text{Re}(\text{CO})_3(\text{C}_4\text{N}_2\text{H}_3\text{S})]_4$  (Fig. 4) has been reported.<sup>44a</sup> The critical issue, however, is whether the X-ray diffraction data for  $[\text{Re}(\text{CO})_3(\text{C}_4\text{N}_2\text{H}_3\text{S})]_4$  could reproduce the structure reported for  $[\text{Cd}(\text{CO})_3(\text{C}_6\text{H}_3\text{Cl})]_4$ , 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  $[\text{Re}(\text{CO})_3(\text{C}_4\text{N}_2\text{H}_3\text{S})]_4$  as the cadmium compound,  $[\text{Cd}(\text{CO})_3(\text{C}_6\text{H}_3\text{Cl})]_4$ . While the positional parameters of the former are available,<sup>44a</sup> the required structure factors have not been reported,<sup>49</sup> and so we collected X-ray diffraction data on  $[\text{Re}(\text{CO})_3(\text{C}_4\text{N}_2\text{H}_3\text{S})]_4$ .

As is evident from Fig. 5, the molecular structure of  $[\text{Re}(\text{CO})_3(\text{C}_4\text{N}_2\text{H}_3\text{S})]_4$  shows a striking resemblance to that for  $[\text{Cd}(\text{CO})_3(\text{C}_6\text{H}_3\text{Cl})]_4$  (Fig. 1).<sup>4</sup> The crystallographic data for  $[\text{Re}(\text{CO})_3(\text{C}_4\text{N}_2\text{H}_3\text{S})]_4$  were, therefore, subsequently refined as  $[\text{Cd}(\text{CO})_3(\text{C}_6\text{H}_3\text{Cl})]_4$  (Fig. 6), which hereafter will be referred to as “ $[\text{Cd}(\text{CO})_3(\text{C}_6\text{H}_3\text{Cl})]_4\text{-Re}$ ” to indicate that the cadmium structure is based on the rhenium data set. Significantly, there is excellent agreement between the respective bond lengths of  $[\text{Cd}(\text{CO})_3(\text{C}_6\text{H}_3\text{Cl})]_4\text{-Re}$  and the published structure of  $[\text{Cd}(\text{CO})_3(\text{C}_6\text{H}_3\text{Cl})]_4$ , 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,  $[\text{Cd}(\text{CO})_3(\text{C}_6\text{H}_3\text{Cl})]_4$ , is actually that of the rhenium compound,  $[\text{Re}(\text{CO})_3(\text{C}_4\text{N}_2\text{H}_3\text{S})]_4$ .

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

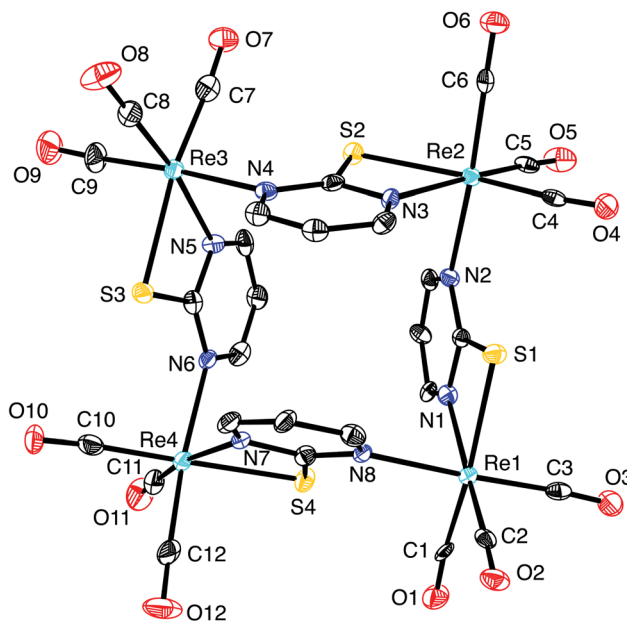


Fig. 5 Atom displacement plot for  $[\text{Re}(\text{CO})_3(\text{C}_4\text{N}_2\text{H}_3\text{S})]_4$  (40% displacement parameters).

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,<sup>50</sup> 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

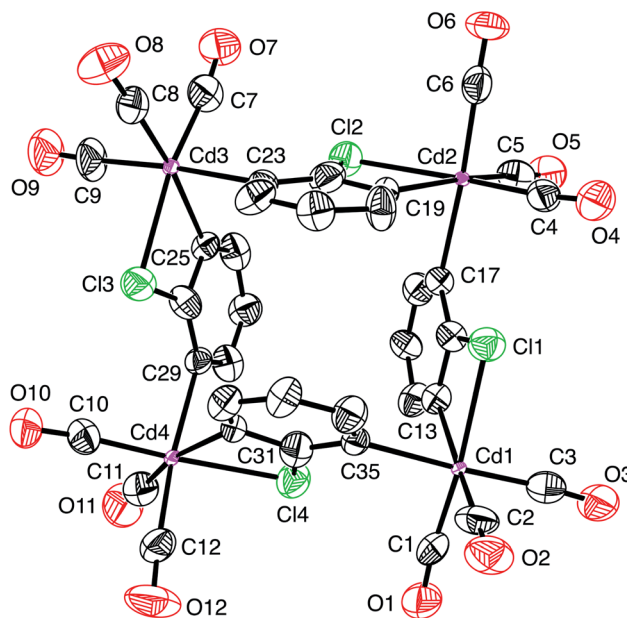


Fig. 6 Atom displacement plot for  $[\text{Cd}(\text{CO})_3(\text{C}_6\text{H}_3\text{Cl})]_4\text{-Re}$  using experimental data for  $[\text{Re}(\text{CO})_3(\text{C}_4\text{N}_2\text{H}_3\text{S})]_4$  (40% displacement parameters).





Fig. 7 Comparison of the bond lengths of  $[\text{Re}(\text{CO})_3(\text{C}_4\text{N}_2\text{H}_3\text{S})]_4$ , refined as  $[\text{Cd}(\text{CO})_3(\text{C}_6\text{H}_3\text{Cl})]_4\text{-Re}$ , with those of the published data for  $[\text{Cd}(\text{CO})_3(\text{C}_6\text{H}_3\text{Cl})]_4$ ,<sup>4</sup> demonstrating an excellent correspondence.

Table 3 Relative average  $U_{\text{eq}}$  values<sup>a</sup> for  $[\text{Re}(\text{CO})_3(\text{C}_4\text{N}_2\text{H}_3\text{S})]_4$ , refined as  $[\text{Cd}(\text{CO})_3(\text{C}_6\text{H}_3\text{Cl})]_4\text{-Re}$ , together with those of the published data for  $[\text{Cd}(\text{CO})_3(\text{C}_6\text{H}_3\text{Cl})]_4$

	$[\text{Cd}(\text{CO})_3(\text{C}_6\text{H}_3\text{Cl})]_4\text{-Re}$	$[\text{Cd}(\text{CO})_3(\text{C}_6\text{H}_3\text{Cl})]_4$ <sup>b</sup>
$U_{\text{eq}}(\text{Cd})_{\text{rel}}$	1	1
$U_{\text{eq}}(\text{C}_{\text{CO}})_{\text{rel}}$	4.80	4.96
$U_{\text{eq}}(\text{O})_{\text{rel}}$	6.43	6.19
$U_{\text{eq}}(\text{Cl})_{\text{rel}}$	4.47	3.87
$U_{\text{eq}}(\text{C}_{\text{CdC}})_{\text{rel}}$	2.89	2.29
$U_{\text{eq}}(\text{C}_{\text{ring}})_{\text{rel}}$	4.25	3.73

<sup>a</sup>  $U_{\text{eq}}(\text{X})_{\text{rel}} = U_{\text{eq}}(\text{X})/U_{\text{eq}}(\text{Cd})$ . <sup>b</sup> 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%.<sup>51</sup> In fact, the CSD contains structures of cadmium compounds with  $R$  values as high as 30.1%.<sup>52</sup> Thus, the  $R$  value for  $[\text{Cd}(\text{CO})_3(\text{C}_6\text{H}_3\text{Cl})]_4\text{-Re}$  cannot be used in the present case as a definitive gauge of an incorrect structure.

Although the  $R$  value for  $[\text{Cd}(\text{CO})_3(\text{C}_6\text{H}_3\text{Cl})]_4\text{-Re}$  does not necessarily indicate an incorrect structure, the small value of  $U_{\text{eq}}$  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  $U_{\text{eq}}$  data for  $[\text{Re}(\text{CO})_3(\text{C}_4\text{N}_2\text{H}_3\text{S})]_4$  and its refinement as the cadmium complex,  $[\text{Cd}(\text{CO})_3(\text{C}_6\text{H}_3\text{Cl})]_4\text{-Re}$ , are compared in Table 4 and Fig. 8. These data indicate that not only is  $U_{\text{eq}}$  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  $U_{\text{eq}}(\text{Cd})/U_{\text{eq}}(\text{Re})$  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

Table 4 Average  $U_{\text{eq}}$  values for  $[\text{Re}(\text{CO})_3(\text{C}_4\text{N}_2\text{H}_3\text{S})]_4$  and the structure refined as  $[\text{Cd}(\text{CO})_3(\text{C}_6\text{H}_3\text{Cl})]_4\text{-Re}$

X	$[\text{Re}(\text{CO})_3(\text{C}_4\text{N}_2\text{H}_3\text{S})]_4$	$[\text{Cd}(\text{CO})_3(\text{C}_6\text{H}_3\text{Cl})]_4\text{-Re}$	$U_{\text{eq}}(\text{X})_{\text{rel}}^a$
M	0.021	0.015	0.71
S/Cl	0.024	0.066	2.75
C <sub>CO</sub>	0.029	0.070	2.41
O	0.044	0.094	2.14
N/C	0.020	0.042	2.10
C <sub>ring</sub>	0.023	0.062	2.70

<sup>a</sup>  $U_{\text{eq}}(\text{X})_{\text{rel}} = U_{\text{eq}}(\text{X})[\text{Cd}(\text{CO})_3(\text{C}_6\text{H}_3\text{Cl})]_4\text{-Re}/U_{\text{eq}}(\text{X})[\text{Re}(\text{CO})_3(\text{C}_4\text{N}_2\text{H}_3\text{S})]_4$ .

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.

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<sup>53</sup> 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 mis-assigned. 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”.<sup>21a-d</sup> 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  $U_{\text{eq}}$  values for all other atoms to increase in



Fig. 8 Comparison of  $U_{\text{eq}}$  values for  $[\text{Re}(\text{CO})_3(\text{C}_4\text{N}_2\text{H}_3\text{S})]_4$  and the structure refined as the cadmium compound,  $[\text{Cd}(\text{CO})_3(\text{C}_6\text{H}_3\text{Cl})]_4\text{-Re}$ . The solid line has a slope of unity and depicts the boundary that indicates whether the  $U_{\text{eq}}$  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.





## Conflicts of interest

There are no conflicts to declare.

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- 70 In addition to the dichloromethane solvate reported here,  $[\text{Re}(\text{CO})_3(\text{C}_4\text{N}_2\text{H}_3\text{S})]_4$  has also been crystallized as an ethanol solvate (ref. 44a) and as a hydrate when reported as  $[\text{Cd}(\text{CO})_3(\text{C}_6\text{H}_3\text{Cl})]_4$  (ref. 4).
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