Element Mis-identification in X-ray Crystallography: A Series of Case Studies

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X-ray crystallography is sometimes described as a definitive technique in identifying a compound. The certainty it offers is really restricted to a description of atom connectivity, as opposed to atom identity, because elements with similar atomic number have similar diffracting power. In this talk, a series of examples are considered in which coordination compounds of the transition metals are incorrectly formulated on the basis of a crystal structure. First, a set of reports describing the syntheses and structures of $[MCl_2(diazadiene)]$ (M = Cr, Mo, W) complexes is reassessed in the context of known chemistry of low-valent Group VI metal complexes, crystallographic trends such as M–Cl bond lengths and unit cell volumes, and calculated metal-ligand bond lengths. Crystallographic data and computational results are inconsistent with any of these species being second or third row transition metal complexes. The crystallographic information files accompanying the $[MCl_2(diazadiene)]$ (M = Mo, W) published structures reveal that the metal atoms were refined with partial site occupancy factors (0.775 for Mo; 0.4005 and 0.417 for W), the effect of which was to produce lighter-element behavior and better refinement in accord with the metal atoms' correct identity, which is Zn^{2+}. Divalent zinc originates from zinc metal employed as a reducing agent. A similar case involving $[(Me_3P)_2ZnCl_2]$ misidentified as $[(Me_3P)_2MoCl_2]$ is noted. A third case of element mis-assignment involves a tetrametallic species, $[M({}^{i}Pr_2Pipdt)]_4[BF_4]_4$ (${}^{i}Pr_2Pipdt$ = diisopropylpiperazine-2,3-dithione), that is created by treatment of $[MoOCl({}^{i}Pr_2Pipdt)_2]^+$ with $AgBF_4$. The metal atom is identified as Mo^{1+}, but a variety of chemical considerations is strongly indicative of Ag^+ as the more chemically plausible metal ion. Finally in our own work, attention is given to considerable confusion caused by the inability to distinguish Cl^- from SH^- as a ligand in Cu^{1+} complexes on the basis of crystallography. Offered in conclusion are thoughts on some preemptive practices that guard against element mis-identification in the crystal structure determination process.

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