



RELOOK ON MERCUROUS NITRITE AND SOME EXOTIC GOLD AND PLATINUM COMPOUNDS

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Evidences seem to indicate that existence of stable mercurous nitrite, reported by P. C. Ray, is doubtful. Ray also reported a number of subnormal compounds of platinum and gold, for which he proposed astounding constitutions, which are most likely to be metal cluster compounds; the plausible structures of a few of these are proposed. Their investigations by X-ray crystallography to determine their structures and thus establish their identity would be fruitful.

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INTRODUCTION

In the year 1896 P. C. Ray reported^{1,2} preparation of mercurous nitrite, $\text{Hg}_2(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$, and during the next few years published a few papers on its preparation and properties.³⁻⁶ He also reported hyponitrites of Hg(I) and Hg(II).⁷⁻¹⁰ Although the reported discovery of mercurous nitrite was highly acclaimed, we hardly notice any mention of this in the advanced level treatises on Inorganic Chemistry published in the following years.

DISCUSSION

In the year 1966 Potts and Allred¹¹ reported that they failed to isolate the mercurous nitrite reported by Ray. Subsequent attempt by the present reporter to make the said compound also ended in failure. On the basis of an estimate of the enthalpy of formation of mercurous nitrite, $\text{Hg}_2(\text{NO}_2)_2$, using thermochemical data available in literature, it was concluded that the compound should be highly endothermic, which explains its instability.¹²

In the year 2009 Hancock and coworkers¹³ reported a stable crown-ether complexed mercurous perchlorate, but the corresponding nitrite was too unstable and disproportionated forming the crown-ether complexed mercury(II) nitrite.

However, Ray reported⁶ that his 'mercurous nitrite' was quite stable and could be crystallized out in a pure form from a hot concentrated aqueous solution, in which it suffered only ca. 20 per cent decomposition (disproportionation) indicating this to be a slow process even in hot water; the recovery of major part of the salt from the solution in a pure form showed that it also did not suffer any hydrolytic transformation. From our knowledge on the

behavior of Hg_2^{2+} and Hg^{2+} ions in solution it seems that the reported hydrolytic stability would suggest the compound to be a basic salt of mercury. Analytical data on the Hg and N contents as reported by Ray¹⁻⁶ agree reasonably well (particularly because of the crude method used in the estimation of Hg) with those expected in basic salts of compositions such as $\text{Hg}_6^1\text{O}(\text{NO}_3)_4 \cdot 2\text{NO}_2$, $\text{Hg}_8^1\text{O}(\text{NO}_3)_6 \cdot 2\text{NO}_2$, $\text{Hg}_2^1\text{Hg}^{\text{II}}_2(\text{OH})_2(\text{NO}_2)_4$, $\text{Hg}_3^1\text{Hg}^{\text{II}}(\text{OH})(\text{NO}_2)_4$ etc.

In view of the aforesaid information and findings the reported determination of the structure of the mercury(I) nitrite of Ray by X-ray crystallography,¹⁴⁻¹⁶ without chemical characterization of its identity, needs reinvestigation after proper chemical characterization of the sample. One group¹⁶ reported the species as unstable requiring work at 100 K; this contradicts what was reported by Ray.⁶

It is worth noting in this connection that the hyponitrites of mercury reported by Ray⁷⁻¹⁰ are even more unlikely to exist.¹⁷

P. C. Ray also reported a series of compounds of platinum and of gold in very abnormal/subnormal valence states for which he proposed astonishingly absurd constitutions.¹⁸⁻²⁴ However, a proper investigation of their structures by sophisticated methods as are available now, including X-ray crystallography, may reveal their true nature, possibly as metal cluster compounds.²⁵⁻²⁸

Thus, for the compound of stoichiometry $2\text{AuCl}_3 \cdot 3\text{C}_2\text{H}_4\text{S}$ (arrived at from analytical data on Au, S and Cl) Ray proposed the constitution shown in Figure 1 in which Ray considered the Au to be in pentavalent state (+5 oxidation state).¹⁹

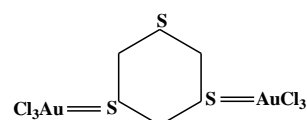


Figure 1. $2\text{AuCl}_3 \cdot 3\text{C}_2\text{H}_4\text{S}$, as proposed by Ray (see text)

However, the proposed constitution is short of 6H from the stoichiometric composition (which of course will not be

distinguishable by analytical data on Au, S and Cl only, due to high molar mass of the species). But assuming that the compound formed was as shown in Figure 1, the S to Au bond would be a coordinate bond with the Au in +3 (and not +5) oxidation state. In fact the compound might be a dinuclear compound of Au^{III} as shown in Figure 2 and Figure 3 having coordination number 5 and 6 respectively for Au(III), examples of which are known²⁹ though rare.

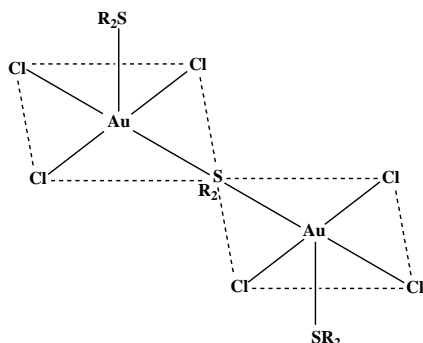


Figure 2. One plausible structure of $2\text{AuCl}_3 \cdot 3\text{R}_2\text{S}$ ($\text{R}_2 = \text{C}_2\text{H}_4$)

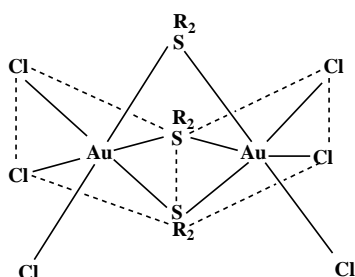


Figure 3. Another plausible structure of $2\text{AuCl}_3 \cdot 3\text{R}_2\text{S}$ ($\text{R}_2 = \text{C}_2\text{H}_4$)

Similarly, the compound $\text{Au}_2\text{Cl}(\text{SCH}_2\text{CH}_2\text{S})_2$ reported by him,¹⁹ for which he proposed the constitution shown in Figure 4 with one Au in bivalent and another Au in trivalent states, is more likely to be a Au-centered trigonal bipyramidal Au₅ cluster with a Cl bound to each of the three Au in the trigonal plane with an $\text{SCH}_2\text{CH}_2\text{S}^-$ ligand bridging two Au along each of six edges of the trigonal bipyramid (Figure 5).

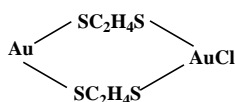


Figure 4. $\text{Au}_2\text{Cl}(\text{SC}_2\text{H}_4\text{S})_2$, as proposed by Ray (see text)

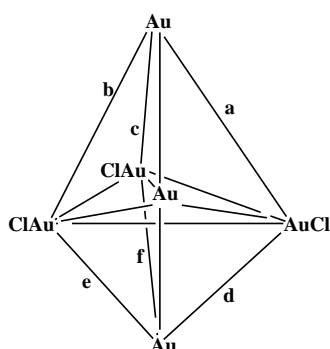


Figure 5. Plausible structure of $\{\text{Au}_2\text{Cl}(\text{SCH}_2\text{CH}_2\text{S})_2\}_3$, i.e. $\text{Au}_6\text{Cl}_3(\text{SCH}_2\text{CH}_2\text{S})_6$. The six $\text{SCH}_2\text{CH}_2\text{S}^-$ ligands are bridging along the edges a-f of the trigonal bipyramid

Likewise, the compound $\text{Pt}_5\text{Cl}(\text{Et}_2\text{S}_2)_4(\text{Et}_2\text{NH})_2$ ²² is likely to be a Cl-centered trigonal bipyramidal Pt₅ cluster with the Et_2S_2 and Et_2NH present as bridging ligands along the edges of the trigonal bipyramid (Figure 6).

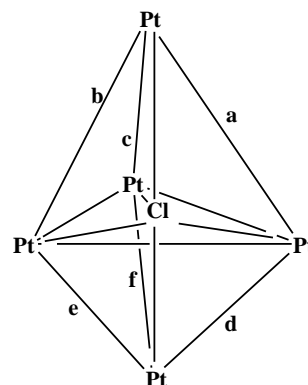


Figure 6. Plausible structure of $\text{Pt}_5\text{Cl}(\text{Et}_2\text{NH})_2(\text{Et}_2\text{S}_2)_4$. The two Et_2NH ligands may be bridging along the edges b and d, while the four Et_2S_2 ligands may be bridging along the edges a, c, e and f.

Elucidation of the structures of all these compounds by X-ray crystallography would be worthy of investigation to establish their true nature. If the last two mentioned compounds are thus shown as metal cluster species, then that would establish P. C. Ray as a pioneer in the field.

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