

be some deviation from an equal distribution of isotope between formate and carbonate, arising from the possibility of an isotope effect in the decomposition of the oxalate ion.

An investigation into the mechanism and preparative use of the exchange, which appears to offer a unique route to labelled formate, and may have implications in other fields, is now in progress, and will be reported elsewhere.

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D. G. GRANT  
H. S. TURNER

Chemical Research Laboratory,  
Teddington, Middlesex.  
Nov. 3.

<sup>1</sup> Melville, D., Rachele, J., and Keller, E., *J. Biol. Chem.*, **160**, 419 (1947).

<sup>2</sup> Gurin, S., Symposium on Use of Isotopes in Biological Research, Univ. Chicago, March 3-4, 1947, quoted by Calvin *et al.*, "Isotopic Carbon", 165 (Chapman and Hall, 1949).

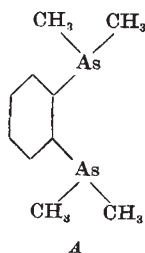
<sup>3</sup> Harman, D., Stewart, T. D., and Ruben S., *J. Amer. Chem. Soc.*, **64**, 2293 (1942).

<sup>4</sup> Cf. Sulzer, *Z. Angew. Chem.*, **25**, 1268 (1912).

<sup>5</sup> *J. Chem. Phys.*, **17**, 589 (1949).

### Trivalent Nickel

WHEN investigating the complexes of bivalent nickel halides with the chelate *o*-phenylene-*bis*-dimethylarsine (*A*)<sup>1</sup>, a series of very stable trivalent nickel salts have been isolated. If an alcoholic solution of nickel chloride is treated with the chelate *A*, a deep blood-red colour develops instantly, and by concentrating the solution a red salt  $[\text{NiA}_2]\text{Cl}_2$  is obtained (found: C, 34.2; H, 4.9; Cl, 10.2;  $[\text{Ni}(\text{C}_6\text{H}_4(\text{As}(\text{CH}_3)_2)_2]\text{Cl}_2$  requires C, 34.3; H, 4.6;



Cl, 10.1 per cent). The compound is diamagnetic with  $\chi = -0.53 \times 10^{-6}$  per gm., hence the cation is planar with the nickel using *dsp*<sup>2</sup> bonds. Attempts were made to convert this salt to the non-ionic complex  $\text{NiA}_2\text{Cl}_2$  by refluxing with hydrochloric acid in alcohol solution. After some hours refluxing in the presence of air, a much less soluble, greenish-yellow substance crystallized out. In large crystals it is brown, but it dissolves in water to a small extent to a greenish-yellow solution. Its analysis agrees with the formula  $\text{NiCl}_3 \cdot 2\text{A}$  (found: C, 32.5; H, 4.5; Cl, 14.3;  $\text{NiCl}_3 \cdot 2\text{C}_6\text{H}_4(\text{As}(\text{CH}_3)_2)_2$  requires C, 32.6; H, 4.3; Cl, 14.4 per cent). The compound can also be prepared by passing chlorine into an aqueous solution of  $[\text{NiA}_2]\text{Cl}_2$ ; the blood-red colour immediately becomes yellow and a yellow powder is precipitated almost quantitatively. An aqueous solution is slowly reduced by sulphur dioxide or stannous chloride and by boiling with hypophosphorous acid, a red solution of the bivalent salt being formed.

The magnetic moment supports the valency of three assigned to the nickel. The compound is paramagnetic with a susceptibility of  $\chi = 1.42 \times 10^{-6}$  per gm. (at 294° K.). After making the necessary correction for diamagnetism, the magnetic moment ( $\mu$ ) is 1.89 Bohr magnetons, corresponding to one unpaired electron, for which theory requires  $\mu = 1.73$ . There is no decomposition after several months, the compound being stable in air, under vacuum and to moisture. When treated with potassium iodide and starch, no blue colour is developed, but the iodide is precipitated. The corresponding bromide and iodide are being investigated.

Jensen and Nygaard<sup>2</sup> have recently described a trivalent nickel complex,  $\text{NiBr}_3 \cdot 2(\text{C}_6\text{H}_5)_3\text{P}$ , in which the nickel atom is five-covalent, and one might have expected the compound described above to be a salt-like analogue, since only part of the chlorine is ionized. However, conductivity measurements suggest that the substance is the octahedral complex  $[\text{NiA}_2]\text{Cl}_2$ , and further potentiometric measurements, which are at present proceeding, seem to confirm this. The compound is remarkable for its stability and ease of formation by aerial oxidation, a reaction which is common with bivalent cobaltamines but hitherto not observed with bivalent nickel. The ease of oxidation by air is explained by the oxidation potential  $[\text{NiA}_2]^{++}/[\text{NiA}_2\text{Cl}_2]^+$ , which is estimated at  $\bar{e} + 0.8$  volt from redox titrations. A more complete discussion of these compounds will appear elsewhere in due course.

The bivalent cobalt complex undergoes similar aerial oxidation. The planar complex  $[\text{CoA}_2]\text{Cl}_2$  (found: C, 33.9; H, 4.6; Cl, 10.1;  $[\text{Co}(\text{C}_6\text{H}_4(\text{As}(\text{CH}_3)_2)_2]\text{Cl}_2$  requires C, 34.2; H, 4.6; Cl, 10.1 per cent; paramagnetic with  $\mu = 2.1$  Bohr magnetons) is oxidized by chlorine or air and hydrochloric acid to a green paramagnetic compound which is obviously not the usual trivalent octahedral complex, since these are invariably diamagnetic. Oxidation of the salt  $[\text{CoA}_2]\text{I}_2$ , however, gives the almost black diamagnetic compound  $\text{CoI}_3 \cdot 2\text{A}$  (found: C, 23.9; H, 3.2;  $\text{CoI}_3 \cdot 2\text{C}_6\text{H}_4(\text{As}(\text{CH}_3)_2)_2$  requires C, 23.7; H, 3.4 per cent), which is undoubtedly the octahedral complex salt  $[\text{CoA}_2\text{I}_2]\text{I}$ . This work is being continued.

R. S. NYHOLM

Sir William Ramsay and  
Ralph Forster Laboratories,  
University College, London.  
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<sup>1</sup> Chatt and Mann, *J. Chem. Soc.*, 610 (1939).

<sup>2</sup> Jensen and Nygaard, *Acta Chem. Scand.*, **3**, 474 (1949).