

## SHORT COMMUNICATIONS

### THE *NN'*-DIHYDRO-1,10-PHENANTHROLINIUM ION\*

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It has been generally believed that protonation of both nitrogen atoms of 1,10-phenanthroline would not be possible because of the proximity of the hydrogen atoms attached to the nitrogen atoms.<sup>1</sup> In the course of investigating phenanthroline chelates of manganese, we isolated the *NN'*-dihydrophenanthroline ion as a salt of the pentachloromanganate(III) ion,  $[\text{phenH}_2][\text{MnCl}_5]$ .<sup>2</sup> This would seem to be the first well-defined compound isolated containing this cation. A previously reported dihydrochloride was not well characterized.<sup>3</sup>

In order to support our claim for the existence of  $[\text{phenH}_2]^{2+}$  in  $[\text{phenH}_2][\text{MnCl}_5]$ , we considered it worthwhile to attempt to isolate other salts containing this cation. It was found that these are readily accessible.

Addition of a solution of 1,10-phenanthroline in 10*N* hydrochloric acid to solutions of cobalt chloride, cadmium chloride, and chloroplatinic acid, also in 10*N* hydrochloric acid, resulted in the crystallization of the anhydrous salts  $[\text{phenH}_2][\text{CoCl}_4]$ ,  $[\text{phenH}_2][\text{CdCl}_4]$ , and  $[\text{phenH}_2][\text{PtCl}_6]$  respectively. These salts show little tendency to lose hydrochloric acid and are, in fact, considerably more stable than  $[\text{phenH}_2][\text{MnCl}_5]$ .

The presence of uncoordinated phenanthroline in these compounds was confirmed by the appearance of a band (unassigned) in their infrared spectra above  $1530\text{ cm}^{-1}$ . This band is confined to the region  $1510\text{--}1530\text{ cm}^{-1}$  in compounds containing coordinated phenanthroline.<sup>4</sup> The band appeared at 1560, 1550, and  $1560\text{ cm}^{-1}$  respectively for the cobalt, cadmium, and platinum derivatives.

It is possible to formulate these compounds in other ways without postulating the existence of  $[\text{phenH}_2]^{2+}$ , e.g. the cobalt and cadmium complexes might be written as  $\text{H}[\text{phenH}][\text{MCl}_4]$  or  $[\text{phenH}][\text{MCl}_3]\cdot\text{HCl}$ . The first formula can be ruled out since there is no likelihood of having a free proton in an anhydrous salt. The cobalt complex can be very easily shown by spectroscopic and magnetic techniques to contain the ion  $[\text{CoCl}_4]^{2-}$ . The complex was found to have a molar susceptibility of 9068 CGS units, giving a magnetic moment of 4.64 B.M. at  $294^\circ\text{K}$ . This lies well within the range expected for tetrahedral cobalt,<sup>5</sup> and is comparable to values

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<sup>1</sup> Brandt, W. W., Dwyer, F. P., and Gyarfas, E. C., *Chem. Rev.*, 1954, **54**, 959.

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<sup>4</sup> Schilt, A. A., and Taylor, R. C., *J. inorg. nucl. Chem.*, 1959, **9**, 211.

<sup>5</sup> Figgis, B. N., and Nyholm, R. S., *J. chem. Soc.*, 1954, 12.

obtained for other salts of  $[\text{CoCl}_4]^{2-}$ .<sup>6</sup> The solid state spectrum (Fig. 1) also confirms the presence of  $[\text{CoCl}_4]^{2-}$ , being virtually identical to that obtained for quinolinium tetrachlorocobaltate(II).<sup>7</sup> It is thus concluded that the cobalt complex isolated can be formulated only as  $[\text{phenH}_2][\text{CoCl}_4]$ , and it therefore seems most likely that the cadmium and platinum complexes, which were prepared using conditions identical to those used for the preparation of the cobalt complex, must also contain the *NN'*-dihydrophenanthroline ion.

It is, perhaps, worth pointing out that attempts at preparation of  $[\text{phenH}_2][\text{AuCl}_4]_2$  by interaction of phenanthroline and chloroauric acid in 10M HCl yielded only  $[\text{phenH}][\text{AuCl}_4]$  which had previously been isolated from solutions approximately 1N in HCl.<sup>8</sup> Failure to isolate  $[\text{phenH}_2][\text{AuCl}_4]_2$  is no doubt related to the greater stability of the crystal lattice of  $[\text{phenH}][\text{AuCl}_4]$ .

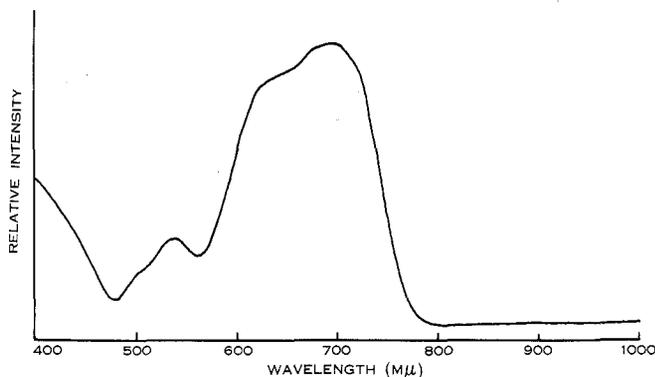


Fig. 1.—Diffuse reflectance spectrum of  $[\text{phenH}_2][\text{CoCl}_4]$  in  $\text{BaSO}_4$ .

### Experimental

The complexes were all prepared by the following method: to a solution of the metal chloride (or chloroplatinic acid) (4 mmole) in 10N HCl (10 ml) was added slowly and with stirring a solution of 1,10-phenanthroline hydrate (4 mmole) in 10N HCl (10 ml). The complex quickly crystallized, was collected, washed successively with 10N HCl, acetone, and ether, and dried *in vacuo* over  $\text{P}_2\text{O}_5$ .

#### (a) *NN'*-Dihydro-1,10-phenanthroline Tetrachlorocobaltate(II)

Blue-green crystals (Found: C, 37.8; H, 2.9; Cl, 37.0; Co, 15.2. Calc. for  $[\text{C}_{12}\text{H}_{10}\text{N}_2][\text{CoCl}_4]$ : C, 37.6; H, 2.6; Cl, 37.0; Co, 15.4%).

#### (b) *NN'*-Dihydro-1,10-phenanthroline Tetrachlorocadmiate(II)

Colourless crystals (Found: C, 33.1; H, 2.3; Cl, 32.7; Cd, 25.9. Calc. for  $[\text{C}_{12}\text{H}_{10}\text{N}_2][\text{CdCl}_4]$ : C, 33.0; H, 2.3; Cl, 32.5; Cd, 25.8%).

#### (c) *NN'*-Dihydro-1,10-phenanthroline Hexachloroplatinate(IV)

Orange crystals (Found: C, 24.0; H, 2.0; Cl, 36.2; Pt, 33.3. Calc. for  $[\text{C}_{12}\text{H}_{10}\text{N}_2][\text{PtCl}_6]$ : C, 24.4; H, 1.7; Cl, 36.1; Pt, 33.1%).

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<sup>7</sup> Holm, R. H., and Cotton, F. A., *J. chem. Phys.*, 1959, **31**, 788.

<sup>8</sup> Harris, C. M., *J. chem. Soc.*, 1959, 682.