630. *The Preparation and Properties of Some Tetrakis(methyl cyanide)copper*(I) *Complexes.*

By B. J. Hathaway, D. G. Holah, and (in part) J. D. Postlethwaite.

The use of metallic copper as a reducing agent is described for the preparation of tetrakis(methyl cyanide) complexes of cuprous tetrafluoroborate, perchlorate, and nitrate. Some properties (molecular weights, conductivities, differential thermal and thermogravimetric analysis and infrared spectra) of the complexes are reported.

After the studies of the reaction between nitrosyl perchlorate and metallic copper in methyl cyanide,[1] where no trace of cuprous species was found, the analogous reaction with nitrosyl tetrafluoroborate has been investigated.[2] In this, a mixture of cuprous and cupric tetrafluoroborate complexes was obtained. The cuprous complex is formed by reduction of the cupric complex by metallic copper, which was first used as a reducing agent by Morgan[3] for the preparation of cuprous chloride- or bromide-mono(methyl cyanide) complexes. This reducing property of copper has now been extended to the preparation of other cuprous complexes.

Experimental

Preparation of Nitrosyl Tetrafluoroborate.[4]—Equivalent amounts of dinitrogen tetroxide and 70—80% fluoroboric acid were mixed at 0° and the precipitate of nitrosyl tetrafluoroborate purified by sublimation under a vacuum at 220°.

Reaction of Copper with Suspensions of Nitrosyl Tetrafluoroborate in Methyl Cyanide.—Powdered nitrosyl tetrafluoroborate (1 g.) was washed with dry ethyl acetate and transferred to a 250 ml. flask closed by a phosphorus pentoxide guard tube. A piece of clean copper sheet (30 × 10 × 1 mm.) and dry methyl cyanide (30 ml.) were added quickly. The flask was immediately evacuated through the guard tube by means of a water pump.[1] Reaction continued with rapid evolution of nitric oxide for about 3 hr., after which the solution was blue-green. The solution was filtered through a No. 4 sintered-glass filter-stick to remove traces of copper and the excess of nitrosyl tetrafluoroborate.

Quantitative tests showed that this solution contained both cuprous and cupric copper. The initial product, cupric tetrafluoroborate, formed by the reaction $2NO^+ + Cu^0 \longrightarrow Cu^{2+} + 2NO$, is partially reduced to cuprous tetrafluoroborate by the copper metal present: $Cu^0 + Cu^{2+} = 2Cu^+$. The latter reaction suggests a useful route to cuprous salts from the corresponding cupric salts, especially as the reduction goes to completion on refluxing.

Preparation of Cuprous Complexes.—The above solution (or one of cupric perchlorate[1] or nitrate in methyl cyanide) was refluxed with copper powder until the solution became colourless. The hot solution was filtered and the cuprous complex which crystallised on cooling was filtered off and dried in a vacuum. The nitrate complex is much less stable than the tetrafluoroborate or perchlorate complex and must be dried in a vacuum for not more than 1 min. if decomposition is to be avoided.

Electrolytic Reduction.—The preparation of the cuprous nitrate complex by electrolysis of cadmium nitrate in methyl cyanide solution at copper electrodes has been reported.[3]

When solutions of cupric tetrafluoroborate or perchlorate were electrolysed with a copper anode and either a copper or platinum cathode, the respective cuprous complexes were formed at the anode, while copper was deposited on the cathode. The cuprous nitrate solvate cannot be prepared by the electrolysis of cupric nitrate in methyl cyanide, since this solution is virtually non-conducting.[5]

Analysis of Solids.—Copper was estimated gravimetrically as copper ethylenediamine mercuri-iodide[6] after oxidation with nitric acid, and the anions as their nitron salts.

---

[1] Hathaway and Underhill, *J.*, 1960, 3705.

[2] Hathaway, Holah, and Underhill, unpublished work.

[3] Morgan, *J.*, 1923, 2901.

[4] Grunther, Balz, Erich, and Mailander, *Z. anorg. Chem.*, 1934, **217**, 161.

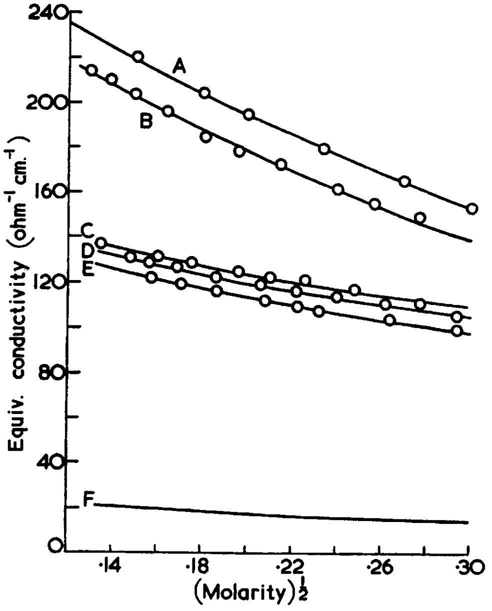
[5] Addison, Hathaway, Logan, and Walker, *J.*, 1960, 4308.

[6] Vogel, " Text Book and Quantitative Inorganic Analysis," Longmans, Green and Co., London, 2nd edn., 1951, p. 433.

Analysis gave the following results. *Cuprous tetrafluoroborate complex*: Cu, 20·2; BF_4, 26·35% ($CuBF_4$,4MeCN requires Cu, 20·2; BF_4 27·6%). *Cuprous perchlorate complex*: Cu, 19·3; ClO_4, 29·6% ($CuClO_4$,4MeCN requires Cu, 19·45; ClO_4, 30·4%). *Cuprous nitrate complex*: Cu, 21·9; NO_3, 22·0% ($CuNO_3$,4MeCN requires Cu, 21·9; NO_3, 21·4%).

Properties of the Cuprous Complexes.—Appearance and melting points. The tetrafluoroborate and perchlorate solvates, m. p. 159—161° and 164—166° respectively, are white crystalline materials which decompose slowly in moist air. The white crystalline nitrate has m. p. 79—81° but decomposes almost immediately in air.

Apparent molecular weights. These were measured ebullioscopically with an apparatus of the Cottrell pump type,[7] methyl cyanide (20 ml.) being the solvent. The pellets were prepared in a small pellet-press in a dry box, and added at intervals down the condenser, closed at other times by a loosely stoppered calcium chloride guard-tube. The temperatures were read through a small telescope (±0·002°). The apparatus was calibrated on Hopkin and Williams's naphthalene ("for molecular-weight measurements"). The variation in the apparent molecular weights of the complexes with concentration is shown in Table 1. The slight increase in the apparent molecular weight of cuprous nitrate may be due to the presence of decomposition products since, when the methyl cyanide solution was cooled after the experiment, a small quantity of amorphous impurity settled out.



Equivalent conductivities in methyl cyanide solution.

A, $Cu(ClO_4)_2$. B, $Cu(BF_4)_2$. C, $Cu(MeCN)_4BF_4$ D, $Cu(MeCN)_4ClO_4$. E, $Cu(MeCN)_4NO_3$. F, $Cu(NO_3)_2$.

TABLE 1. *Apparent molecular weights in methyl cyanide.*

$CuBF_4$,4MeCN				$CuClO_4$,4MeCN				$CuNO_3$,4MeCN			
Mol. wt.	Molarity	Mol. wt.	Molarity	Mol. wt.	Molarity	Mol. wt.	Molarity	Mol. wt.	Molarity	Mol. wt.	Molarity
70	0·026	77	0·063	79	0·037	84	0·073	73	0·037	74	0·089
72	0·036	78	0·072	82	0·047	84	0·080	72	0·050	74	0·099
73	0·045	77	0·098	84	0·056	86	0·100	72	0·061	77	0·119
76	0·052	78	0·119	84	0·065	86	0·111	72	0·079	78	0·131

Over the concentration range studied the apparent molecular weights indicate that all the compounds are completely dissociated: $CuX \longrightarrow Cu^+ + X^-$. The values for cuprous nitrate are in complete contrast to the molecular weights of cupric nitrate in methyl cyanide,[5] which has been shown to be monomeric over this concentration range.

Molecular conductivities in methyl cyanide. These were measured by using a Cambridge

---

[7] Cottrell, *J. Amer. Chem. Soc.*, 1919, **41**, 721.

conductivity apparatus involving a 1000 cycles/sec. oscillator and a galvanometer as a null point instrument. The cell design was that of Groenevald and Zuuv,[8] which enables measurements to be made on hygroscopic solutions under a dry atmosphere.

The variations of molar conductivities with square root of molar concentrations are shown in Fig. 1. The conductivities of the three cuprous compounds are very close, all indicating complete dissociation of a 1 : 1 electrolyte, and agreeing with the molecular weights. The normal Onsager type equation is obeyed, although the plot of Λ against $\sqrt{c}$ is not exactly linear.

These values are compared with those obtained for cupric tetrafluoroborate[2] and perchlorate,[1] both of which show conductivities typical of a 2 : 1 electrolyte. The conductivity of cuprous nitrite is similar, but differs from that of the cupric compound which has a very low conductivity.[5]

Differential thermal analysis. The sample (0·1 g.) was contained in a small ignition tube into which dipped one terminal of a thermocouple, packed in position with glass wool. The other terminal was placed in a similar ignition tube containing powdered silica. Both the small tubes and a thermometer were contained in a B.24 tube placed in a vertical electric furnace. The thermocouple terminals were connected to a millivoltmeter, and the furnace current adjusted manually to give a heating rate of 3°/min. When the observed e.m.f. was recorded against the temperature, the cuprous tetrafluoroborate solvate showed only an endothermic peak, at 168°, corresponding to the m. p., indicating that endothermic decomposition probably occurs at the m. p. The perchlorate solvate showed clearly the endothermic m. p. at 175°, followed by explosive decomposition at 205°. A weak endothermic peak corresponding to the m. p. of the nitrate occurred at 95° and a weak endothermic peak at 138° is probably due to partial decomposition of the nitrate. Exothermic decomposition occurred at 141° owing to oxidation of methyl cyanide by nitrate ion, but the origin of a weak exothermic peak at 220° is unknown.

TABLE 2. *Infrared absorption frequencies* (cm.$^{-1}$).

$CuNO_3$,4MeCN	$Cu(NO_3)_2$	$CuBF_4$,4MeCN	KBF_4	$CuClO_4$,4MeCN	$KClO_4$
771w	770s	777w	773vw	779w	
	787s, b 795s, sh	789m, sp			
798m, sp					
815vw					
833vw					
	907w				
				925 945 } w, sh	927vw
1022m, sp	1016m, sh	1032 1125 } vs, b	1038 1128 } vs, b	1090 1150 } vs, b	1110vs, b
1040m, sh	1038s, b				
1168w					
1300vs, sp	1264vs, b 1289vs, sh	1290w		1310vw	
1345m	1344vs		1312vw		
	1504m, sp		1330vw	1370w	
	1546vs	1600vw	1623 1671 } vw		
	1565vs				2050w
	1592vs, sp				
2270 2290 } split		2270 2290 } split		2275 2300 } split	

Thermogravimetric analyses. These were carried out on a Stanton thermo-recording balance at a heating rate of 2°/min. The sample was contained in a small tube and an atmosphere of dry nitrogen maintained in the furnace. The weight loss (%) was recorded against temperature. Thermogravimetric analyses were carried out on the nitrate and tetrafluoroborate complexes, but not on the perchlorate because of its thermal instability.

With both complexes there is a gradual loss of methyl cyanide, followed by a much more rapid loss when anion oxidation of the methyl cyanide occurs. In neither case was any evidence for a stable intermediate obtained. Decomposition of the nitrate was complete by 160° and of the tetrafluoroborate by 270°, emphasising the lower thermal stability of the former. The

---

[8] Groenveld and Zuuv, *Rec. Trav. chim.*, 1953, **72**, 618.

decomposition temperatures agree fairly well with the data from the differential thermal analysis. The total weight loss of the nitrate was 75·2% (decomposition to cupric oxide requires 72·5%) and for the tetrafluoroborate was 75·6% (decomposition to cupric oxide requires 74·7% and to cupric fluoride requires 67·8%).

These results show that the anhydrous cuprous salts cannot be prepared from their complexes, Even the use of low-temperature decomposition under a vacuum in the case of the nitrate failed to yield a compound of definite composition.

Infrared spectra. The spectra were determined for Nujol mulls in a Unicam S.P. 100 spectrophotometer. The main infrared absorption frequencies of the cuprous complexes are given in Table 2. The spectra of the tetrafluoroborate and perchlorate complexes are very similar to those of an ionic tetrafluoroborate [9] and perchlorate.[10] This evidence for the ionic nature of the complexes is consistent with molecular weights and molar conductivities in solution. The spectrum of the cuprous nitrate complex is very similar to that of cupric nitrate [11] which has been shown to contain nitrato-groups, and this strongly suggests that the solid complex also contains this group. The behaviour in methyl cyanide solutions, however, indicates complete dissociation to cuprous and nitrate ions, so the co-ordination is much weaker than in cupric nitrate.

The split absorptions at 2270—2300 cm.$^{-1}$ in the complexes are due to the $-C\equiv N$ vibration, which is shifted to slightly higher frequencies than the normal one at 2248 cm.$^{-1}$ in methyl cyanide. This is consistent with co-ordination of methyl cyanide to copper,[12] but does not distinguish between the strength of co-ordination of the tetrafluoroborate and perchlorate complexes and the less stable nitrate.

DISCUSSION

The empirical formulæ of the complexes suggest that the cuprous ions are four co-ordinated, with the four molecules of methyl cyanide probably occupying the stereochemically preferred tetrahedral positions.[13,14] In solution there is no evidence to indicate that the cation is other than the tetrahedral tetrakis(methyl cyanide)copper(I), and a simple tetrafluoroborate, perchlorate, or nitrate anion. Although the solution properties are very similar, the very low thermal stability of the nitrate complex must be explained. The nitrate ion as well as being smaller, is a flat trigonal ion as opposed to the essentially spherical tetrafluoroborate and perchlorate ions.[15] It also has a greater tendency to co-ordinate than the other two.[11,16] In the solid complex the nitrate ion may therefore approach (between two of the tetrahedrally co-ordinated methyl cyanide molecules) sufficiently close to the cuprous ion to form a weak copper to nitrate bond. This accounts for the infrared spectra; further, the close approach of the nitrate ion may distort the tetrahedral distribution of the methyl cyanide molecules, leading to the observed instability.

The authors are indebted to Dr. G. W. Gray for the infrared measurements, to the Chemical Society for a grant for apparatus, and to the Department of Scientific and Industrial Research for a maintenance grant (to D. G. H.).

THE UNIVERSITY, HULL. [*Received, February 22nd*, 1961.]

---

[9] Greenwood, *J.*, 1959, 3811.
[10] Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.
[11] Addison and Gatehouse, *J.*, 1960, 613.
[12] Coerver and Curran, *J. Amer. Chem. Soc.*, 1958, **80**, 3522.
[13] Mann, Purdie, and Wells, *J.*, 1936, 1503.
[14] Cotton and Goodgame, *J.*, 1960, 5267.
[15] Bowen, Donohue, Jenkin, Kenward, Wheatley, and Whiffen, *Chem. Soc. Special Publ.* No. 11, 1958.
[16] Gatehouse, Livingstone, and Nyholm, *J.*, 1957, 4222.