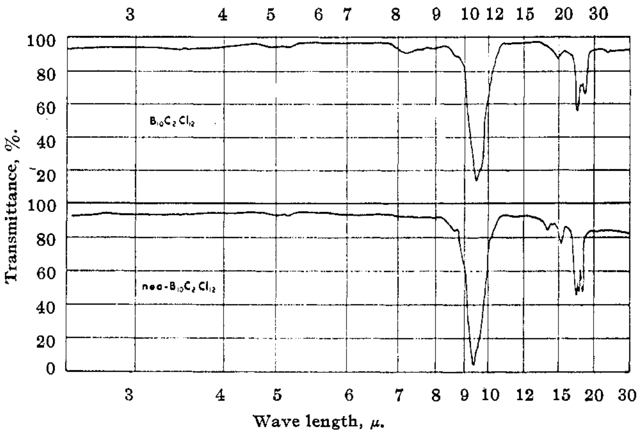
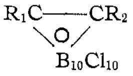


Fig. 1.—Infrared spectra of perchlorocarborane and perchloroneocarborane (KBr pellet).

TABLE I

^{11}B N.M.R. CHEMICAL SHIFTS OF DECACHLOROCARBORANE, DECACHLORONEOCARBORANE, AND DERIVATIVES IN P.P.M. FROM EXTERNAL METHYL BORATE

R_1	R_2	Low-field singlet	High-field singlet (A)	High-field singlet (B)	
H	H	16.8	28.0		 R_1C——CR_2 \O/ $B_{10}Cl_{10}$
CH_3	H	16.1	27.4		
C_2H_5	H	17.5	27.3		
CH_3	CH_3	16.8	26.9		
C_2H_5	C_2H_5	17.8	26.3		
Cl	Cl	20.0	27.6		
H	H	21.8	27.3	31.4	$R_1CB_{10}Cl_{10}CR_2$
CH_3	CH_3	21.3	27.9	...	
C_2H_5	C_2H_5	21.5	27.0	...	
Cl	Cl	20.6	28.2	...	

pounds consists of two singlets (intensity ratio 2:8), the chemical shifts of which are presented in Table I. While the high-field chemical shifts are nearly identical in all compounds, the low-field shifts of m-$B_{10}Cl_{10}C_2(CH_3)_2$ and m-$B_{10}Cl_{10}C_2(C_2H_5)_2$ readily distinguish them from the corresponding carborane compounds. This strongly indicated that during the preparation and reaction of m-$B_{10}Cl_{10}C_2Li_2$ no reversion to the o-carborane structure occurs.

Additional evidence for differentiating the perchloro isomers was gained by examining their far-infrared spectra up to 30 μ (Fig. 1), which clearly differ in the position and relative intensity of characteristic triplet absorptions between 17 and 18.3 μ. Final evidence was obtained by differential scanning calorimetry, which showed that o-$B_{10}C_2Cl_{12}$ is transformed into m-$B_{10}C_2Cl_{12}$ at 380°. At this temperature a distinct exothermic reaction occurred and the sample recovered displayed the characteristic m-$B_{10}C_2Cl_{12}$ absorptions in the far-infrared.

Although both ^{11}B n.m.r. shifts of the carborane derivatives are positioned as expected, in the neocarborane series the third peak (singlet B) shown by m-$B_{10}Cl_{10}C_2H_2$ at 31.4 p.p.m. is obviously absent in its dimethyl, diethyl, and dichloro derivatives. Apparently, substituents other than hydrogen at the carbon atoms of m-$B_{10}Cl_{10}C_2H_2$ effect the movement of the high-field singlet B to coincide with the high-field singlet A, the intensity of which is proportionately increased. Since two boron atoms (2, 3) (see Fig. 2) would be primarily influenced by any change occurring at the carbon atoms, we suspect that the high-field singlet B at 31.4 p.p.m. in m-$B_{10}Cl_{10}C_2H_2$, as well as the high-field doublet (centered at 32.6 p.p.m.) in neocarborane,[2] arise from these atoms.

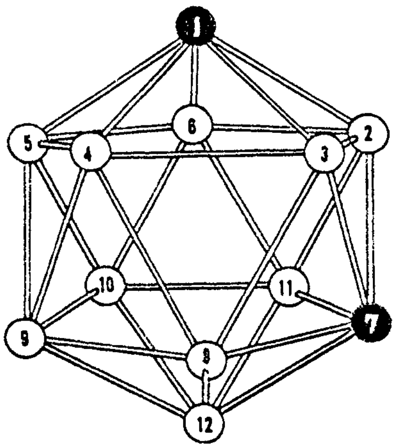


Fig. 2.—Neocarborane skeleton.

These observations emphasize the fact that the interpretation of ^{11}B n.m.r. spectra of C,C′-substituted neocarboranes requires further exploration.

Acknowledgment.—We wish to thank Dr. A. P. Gray for recording the far-infrared spectra and conducting the calorimetry experiments. Also we are indebted to Mr. G. D. Vickers for obtaining the ^{11}B n.m.r. spectra. This work was supported by the Office of Naval Research.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF NEW YORK, STONY BROOK, NEW YORK

Electronic and Magnetic Properties of $K_3Cu(NO_2)_5$

BY IVAN BERNAL

Received March 31, 1964

To our knowledge, the literature does not contain electron spin resonance measurements on a pentacoordinated compound of copper. The number of well-substantiated examples of copper in this environment is small, and the only example where the five ligands are the same is $[Co(NH_3)_6]CuCl_5$.[1] Unfortunately, this compound is not very useful for e.s.r. work since it contains 32 molecules in the unit cell. Furthermore, it is not soluble in solvents convenient to study the substance in a glass. The structure of $NH_4Cu(NH_3)_5(ClO_4)_3$[2] has now been shown to be made up of

---

(1) M. Mori, Y. Saito, and T. Watanabe, *Bull. Chem. Soc. Japan*, **34**, 295 (1961).

(2) M. Buskovska and M. A. Porai-Koshits, *Kristallografiya*, **5**, 140 (1960); **6**, 381 (1961).

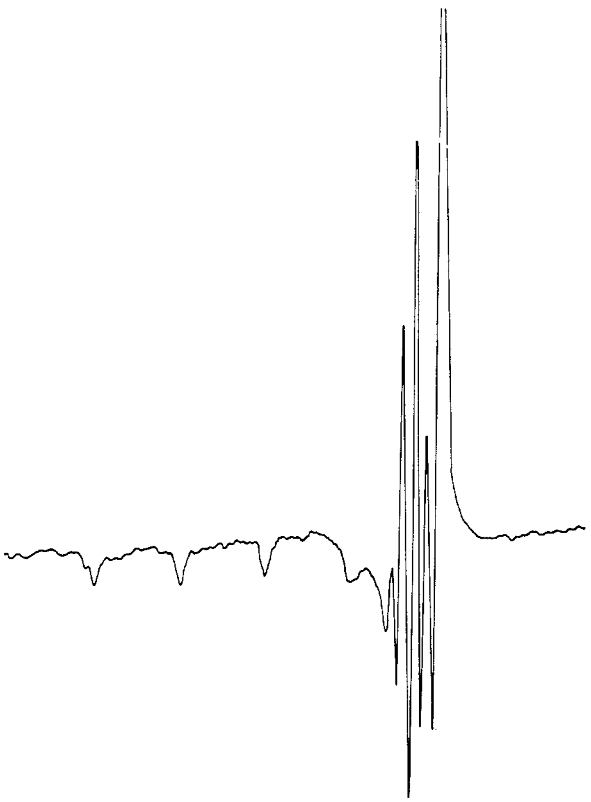


Fig. 1.—Electron spin resonance of $K_3Cu(NO_2)_5$ in DMF–ethanol at liquid nitrogen temperature. Magnetic field increases from left to right; scale: 1 in. = 144 gauss.

$Cu(NH_3)_4^{2+}$ units. Finally, the compounds reported by Harris, *et al.*,[3] by Barclay,[4] and by Carbridge[5] contain bulky ligands that may force pentacoordination upon the ion.

Experimental

Synthesis of $K_3Cu(NO_2)_5$.—Kurtenacker[6] prepared $K_3Cu(NO_2)_5$ and also the Rb and Cs salts. On the basis of elemental analysis he formulated the compound as a monomer. We have prepared this compound as black-green needles, m.p. 163°. *Anal.* Calcd.: N, 17.05. Found: N, 17.01. The compound has been characterized further by the following physical measurements.

Optical Spectrum.—A dry methanol solution, made immediately before recording the spectrum in a Cary Model 14 spectrophotometer, yields a single broad band centered at 14,200 cm.$^{-1}$, with a half-width of about 7000 cm.$^{-1}$. This band can be decomposed into three gaussian components[7] centered approximately at 9700, 12,000, and 17,000 cm.$^{-1}$.

Infrared Spectrum.—Recorded in a Perkin-Elmer Model 21 spectrophotometer using NaCl optics and mull techniques. The principal bands are at 1350, 1210, and 816 cm.$^{-1}$, which are probably the ν_3, ν_1 stretch and the NO_2 bend, respectively. This spectrum has already been described by Gillard and Wilkinson[8] in detail. They also found three weak bands at about 450 cm.$^{-1}$ which they assign to M–NO_2 wagging modes and which will be discussed below.

X-Ray Diffraction.—Single-crystal X-ray measurements were made with the aid of Mr. T. Jordan at Professor W. N. Lipscomb's Laboratory. The results are in agreement with the recent unit cell measurements of Ferrari, *et al.*[9]

The results below were obtained from precession and Weissenberg oscillation photographs: $a = 21.74$, $b = 18.96$, $c = 10.87$ Å.; d(measd.) = 2.46, d(calcd.) = 2.43 g./cc.; $z = 16$. Systematic absences for $0kl$ for $k = 2n$ and $h0l$ with $h + l = 2n$ indicate that the probable space group is either $D_{2h}(16)$ or $C_{2v}(9)$, as was found by Ferrari, *et al.*[9]

Susceptibility.—The susceptibility of the compound was measured in a Gouy balance at 21°. The average magnetic moment per Cu^{2+} ion for two packings is 1.95 ± 0.04 B.M., in good agreement with the results of Gillard and Wilkinson.[8]

Electron Spin Resonance.—A dry ethanol–DMF solution was prepared and immediately frozen in liquid N_2. The frozen glass thus obtained gives the e.s.r. spectrum in Fig. 1. The spectrum was recorded in a Varian 4502 spectrometer using 100 kc./sec. field modulation. Field positions were obtained from strip chart recordings, a Harvey-Wells 502 gaussmeter, and a Hewlett-Packard counter.

The spectrum shows distinctly the two sets of lines expected for an axial complex. Analysis of the spectrum using the equations of Kivelson[10] gives $A = 183$ gauss, $B = 38$ gauss, $g_{\|} = 2.30$, and $g_{\perp} = 2.04$.

Discussion

The average magnetic moment of an axial copper compound can be calculated from the anisotropic g-factors and the approximate expression

$$\mu = 2.83\left[\frac{N\beta^2}{12k}(g_{\|}^2 + 2g_{\perp}^2)\right]^{1/2}$$

where the high-frequency terms of the correct expression have been omitted. The result obtained is 1.92 B.M., in satisfactory agreement with the value measured with a Gouy balance. This result implies that the e.s.r. data taken in the ethanol–DMF glass are relevant to the solid complex, and that the solvent has not altered the metal complex to any appreciable extent.

The elemental analysis, the infrared spectrum, and the X-ray measurements indicate that the compound is anhydrous with a composition $K_3Cu(NO_2)_5$ or a multiple thereof. The absence of a band at 1485 cm.$^{-1}$ suggests[11,12] that there are no asymmetric bridging nitrite groups in the crystal. Certain splittings observed by Gillard and Wilkinson[8] have been suggested as evidence for two types of NO_2^- groups, as expected from an axial complex. However, although no distinction between trigonal bipyramid or square pyramid was made, these authors dismiss the possibility of having bridging nitrite groups; *i.e.*, sixfold coordination by polymerization. They also tentatively assigned the weak vibrations at about 450 cm.$^{-1}$ to M–NO_2 wagging modes.

The relative magnitudes of the two spectroscopic splitting factors show that the complex has to be axially elongated. Otherwise, Griffith has shown[13] that for axial compression $g_{\|} = 2.000 < g_{\perp}$. Using the equa-

---

[3] C. M. Harris, T. N. Lockyer, and H. Waterman, *Nature*, **192**, 424 (1961).

[4] G. A. Barclay and C. H. L. Kennard, *ibid.*, **192**, 425 (1961).

[5] D. E. C. Carbridge and E. G. Cox, *J. Chem. Soc.*, 594 (1956).

[6] A. Kurtenacker, *Z. anorg. allgem. Chem.*, **82**, 204 (1913).

[7] R. L. Belford, M. Calvin, and G. Belford, *J. Chem. Phys.*, **26**, 1165 (1957). See their spectrum of bis(3-ethylacetylacetonato)copper(II) in CH_3OH.

[8] R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 5399 (1963).

[9] A. Ferrari, M. Nardelli, and G. Bigliardi, *Gazz. chim. ital.*, **88**, 827 (1958).

[10] R. Neiman and D. Kivelson, *J. Chem. Phys.*, **35**, 156 (1961).

[11] K. Nakamoto, J. Fujita, and H. Murata, *J. Am. Chem. Soc.*, **80**, 4817 (1958).

[12] B. Gatehouse, *J. Inorg. Nucl. Chem.*, **8**, 79 (1958).

[13] J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, 1961, p. 343.

tions of Griffith[13] for an axially elongated Cu^{2+} complex and the optical data, we calculate $g_{\parallel} = 2.30$ and $g_{\perp} = 2.09$ if we use Gerritsen's[14] value of -660 cm.$^{-1}$ for the spin–orbit coupling constant.

The e.s.r. spectrum shows no nitrogen ligand hyperfine interaction which means either that (a) the complex has weak Cu–N interaction, (b) the ligand orbitals admixed to the metal ligand orbitals have no nitrogen s-orbital character, or (c) the metal is complexed by the NO_2^- oxygens. Gillard and Wilkinson[8] rule (c) out on the basis of the infrared spectrum, although the reason given actually excludes only M–N–O–M bridging nitrites. The possibility that choice (b) is correct offers interesting implications about the geometry of the complex but we do not feel that the data available warrant these speculations. Choice (a) seems to be preferred on the basis of the $Cu–NO_2$ wagging bands at about 450 cm.$^{-1}$ observed by Gillard and Wilkinson.[8] Fujita, *et al.*,[11] measured the M–N wag for a number of nitrite complexes and concluded that there was good correlation between the position of this band and the strength of the M–N band. Consequently, it appears that this is a weakly complexed copper—an idea that seems to be supported by the instability of this complex, but not by the molecular parameters derived from the e.s.r. spectrum. In order to calculate molecular bonding parameters for $K_3Cu(NO_2)_5$ from e.s.r. data, one needs to know the energies of the $xy \rightarrow x^2–y^2$ and $z^2 \rightarrow x^2–y^2$ transitions. Our values are 9700 and 12,000 cm.$^{-1}$, respectively, which are similar to those in anhydrous $Cu(NO_3)_2$.[15] Using the equations of Neiman and Kivelson[10] and the anisotropic e.s.r. data one obtains $\alpha = 0.81$, $\beta_1^2 = 0.67$, and $\beta^2 = 0.51$; where α, β_1, and β are molecular parameters that characterize the in-plane σ-bonding, in-plane π-bonding, and out-of-plane π-bonding, respectively. For comparison, anhydrous $Cu(NO_3)_2$, also studied in a glass,[15] gives $\alpha^2 = 0.6$, $\beta_1^2 = 0.9_6$, and $\beta^2 = 0.8_8$. These results mean the σ-bonds in anhydrous $Cu(NO_3)_2$ are much stronger than in $K_3Cu(NO_2)_5$, while the opposite is true for the π-bonds. The value for β^2 is the least reliable of the parameters given, since it depends on two quantities, $g_{\perp}$ and ΔE_{xz}, known to be unreliable. The other two results are more trustworthy and similar to the relevant values in copper phthalocyanine.[10] This latter observation is worth contrasting with the foregoing results of Gillard and Wilkinson[8] based on the assignment of the $Cu–NO_2$ wagging modes.

Conclusions

(1) The absence of an infrared band at 1485 cm.$^{-1}$ suggests that this compound may be pentacoordinated. However, the validity of this criterion is not well established and its negative aspect is disturbing.

(2) Magnetic, optical, and e.s.r. data have been shown to be self-consistent and demonstrate only that the complex has to be axially elongated. No further data can be derived about the geometry from the results. It is unfortunate that the N ligand hyperfine splittings could not be observed to determine the number of nitrogen ligands. Further work using other glasses is in progress since it may be possible to achieve better resolution in other media.

(3) The absence of nitrogen ligand hyperfine splitting and the Cu–N wagging band at 450 cm.$^{-1}$ indicate that the NO_2^- groups act as weak ligands in this case. These results, however, are in contrast with the molecular parameters derived from the e.s.r. measurements and with the known ability of NO_2^- ligands to give low-spin Co^{2+} complexes.[16,17]

Acknowledgment.—The author wishes to thank Professor W. N. Lipscomb and Mr. T. Jordan for aid and advice concerning the X-ray measurements, Dr. R. H. Holm for the use of his Gouy balance, and Dr. A. H. Maki for helpful advice while the author was at Harvard University. This work was partially supported by a National Science Foundation Grant to Dr. Maki.

---

[14] H. J. Gerritsen and A. Starr, *Arkiv Fysik*, **25**, 13 (1963).

[15] S. J. T. Owen, K. J. Standley, and A. Walker, *J. Chem. Phys.*, **40**, 183 (1964).

[16] B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 400.

[17] P. Ray and H. Sahu, *J. Indian Chem. Soc.*, **23**, 1233 (1947).

CONTRIBUTION FROM THE CHEMICAL ENGINEERING
LABORATORY, CALIFORNIA INSTITUTE OF
TECHNOLOGY, PASADENA, CALIFORNIA

Electron Spin Resonance Studies of Sodium Dithionite and Sodium Formaldehyde Sulfoxylate

BY R. G. RINKER, T. P. GORDON, AND W. H. CORCORAN

Received April 24, 1964

To provide information on the structure of sodium formaldehyde sulfoxylate in aqueous solution with particular relation to sodium dithionite, studies were made which are reported here. E.s.r. spectra of an aqueous solution of sodium dithionite, of solid sodium dithionite, and of an acidified sodium formaldehyde sulfoxylate solution are compared and discussed.

Experimental

In the preparation of the sodium formaldehyde sulfoxylate, material from Eastman Kodak with a melting point of 65° was recrystallized at about 0° from a water–methanol solution and dried at 50° under vacuum. The dry powder was used to prepare saturated solutions at room temperature in pure water, 1 *M* NaOH, and 1 *M* HCl. Sample tubes of Pyrex were filled with each solution. Tubes of sodium dithionite in aqueous solution and in powder form were prepared as previously noted.[1]

A calibration tube was made using a 0.1 *M* solution of manganous chloride in order to compare the resonance signals of the prepared samples with known values of the splitting factor and the gauss separation between resonance peaks for the free

---

[1] R. G. Rinker, T. P. Gordon, D. M. Mason, and W. H. Corcoran, *J. Phys. Chem.*, **63**, 302 (1959).