

TABLE IV
 WATER AND THIOCYANATE EXCHANGE DATA

System	k_1 (25°), sec ⁻¹	ΔH^* , kcal/mole	ΔS^* , cal/mole deg	A/h , cps
$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}-\text{H}_2\text{O}^{17}$ ^a	2.7×10^4	11.6	0.6	4.3×10^7
$[\text{Ni}(\text{NCS})_4(\text{H}_2\text{O})_2]^{2-}-\text{H}_2\text{O}^{17}$ ^b	1.1×10^6	6.0	-11	2.0×10^7
$[\text{Ni}(\text{NCS})_4(\text{H}_2\text{O})_2]^{2-}-\text{H}_2\text{O}^{17}$ ^c	ca. 1.5×10^6	7.4	-5	ca. 3×10^7
$[\text{Ni}(\text{NCS})_4(\text{H}_2\text{O})_2]^{2-}-\text{NCS}^-$ ^b	5.3×10^6	9.2	-1	2.2×10^7 (N ¹⁴)

^a T. W. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962). ^b Ca. 8.0 M KNCS. ^c Ca. 3.5 M NaNCS, 4.5 M NaClO₄.

exchange. It would, of course, be desirable to have some independent method to check on the rate data. Assuming that the results are correctly interpreted, there seems to be no way of distinguishing between processes involving independent water and thiocyanate exchange with the same species of nickel complex or with independent processes involving different nickel species. The predominant species are not necessarily the kinetically significant ones. The shift data, however would be more difficult to reconcile with effects due to minor species, requiring rather large values for the scalar coupling constants. We plan to turn to systems which seem to be better defined, such as the Ni^{II}·NH₃(aq) and Co^{II}·NH₃(aq) complexes, in order to pursue these exchange studies and to see how general such results are. Use of higher O¹⁷ enrichments and higher magnetic fields will be of considerable aid in obtaining more precise data.

Some data for comparisons are collected in Table IV. Substitution of water by thiocyanate in $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ appears to labilize the remaining water with a quite large decrease in ΔH^* . It may be that a *trans*-tetra-

thiocyanatodiaquonickel species with stretched Ni-O bonds is involved. This idea is consistent with the lower A/h value per water molecule in the substituted species. A plot of ΔH^* vs. A/h for the water data is linear (including the origin). This fact may not be significant but is consistent with the notion that replacement of water by thiocyanate results in weaker bonding (due to stretched bonds) with the remaining water.

We do not attach a large amount of significance to the NaNCS-NaClO₄ data as they are limited in number, and uncertainties about species and medium effects are considerable. The apparent difference in ΔH^* between the 8 M KNCS and the 3.5 M NaNCS-4.5 M NaClO₄ mixtures might be real and due to the importance of species such as the trithiocyanato at lower thiocyanate concentration. More work is needed before such effects can be clearly understood.

It seems to us rather significant that the water and thiocyanate exchanges should proceed independently and that further studies of this general nature will be of great interest in this field.

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Bonding in Crystalline Potassium Dicyanocuprate(I)^{1,2}

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Using the known structure of $\text{KCu}(\text{CN})_2$ and the experimentally determined electric field gradient tensor components and asymmetry parameter a model of the bonding, using sp²-hybrid σ -bonding orbitals and d- π^* bonding, is developed. This model shows substantial agreement with experimental evidence. Other possible contributions to the bonding are discussed and their omissions justified.

Introduction

The determination of the components of the electric field gradient (EFG) tensor and asymmetry parameter at the copper nuclei,³ the assignment of the infrared and Raman spectra,⁴⁻⁶ and the previously determined crystal structure⁷ of potassium dicyanocuprate(I),

(1) This work was supported by a grant from the National Science Foundation.

(2) Presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

(3) G. L. McKown and J. D. Graybeal, *J. Chem. Phys.*, **44**, 610 (1966).

(4) G. Moreau, H. Poulet, and J. P. Mathieu, *Bull. Soc. Franc. Mineral. Crist.*, **88**, 6 (1965).

(5) M. J. Reinfeld and L. H. Jones, *J. Mol. Spectry.*, **18**, 222 (1965).

(6) D. Cooper and R. A. Plane, *Inorg. Chem.*, **5**, 16 (1966).

$\text{KCu}(\text{CN})_2$, have provided a sufficient experimental basis for the development of a model for the bonding in the compound. The first prediction of the type bonding in $\text{KCu}(\text{CN})_2$ was by Kruger and Meyer-Berkhout⁸ following their initial observation of the nuclear quadrupole resonance (nqr) spectrum of a polycrystalline sample. Their assumption was that of a structure containing linear (NC-Cu-CN) units in which the Cu atom employed p_zd_z-hybrid orbitals for bonding. The subsequent crystal structure determination has shown this to be incorrect. The dia-

(7) D. T. Cromer, *J. Phys. Chem.*, **61**, 1388 (1957).

(8) H. Kruger and U. Meyer-Berkhout, *Z. Physik*, **132**, 171 (1952).

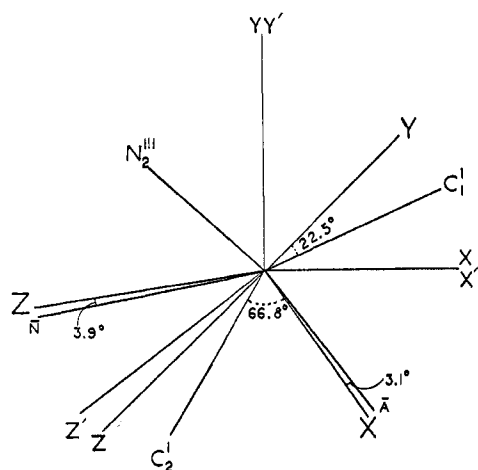


Figure 2.—Relationship of EFG axis system (X, Y, Z), crystal axis system (x', y', z'), and bond directions to the reference axis system (x, y, z).

There are several noteworthy features about the collected data which forms the basis for the discussion which follows: (1) The Cu-C bond lengths, 1.916 and 1.922 Å, are longer than those predicted by the Schomaker-Stevenson relation using normal covalent radii and electronegativities, 1.86 Å. This is a trend noted in the limited studies available for other copper(I) coordination compounds.⁹⁻¹¹ (2) The Cu-N bond length, 2.052 Å, is longer than that predicted from covalent radii and electronegativities, 1.82 Å, and the Cu-N-C bond angle, 139.1° , deviates markedly from linearity. (3) The configuration of the three atoms bonded to the Cu atom is approximately trigonal with the normal, \bar{n} , to the plane of the C_1^I -Cu- C_2^I atoms nearly coinciding with the principal EFG Z axis. (4) Comparison of the CN stretching frequencies with those in other inorganic cyanides¹² shows that they lie on the low side of the observed spread, indicating a weakening of the $C\equiv N$ bond, while comparison of the Cu-CN stretching frequencies shows a high value, indicating an increase in bonding. (5) The EFG asymmetry parameter is very large.

A model of the bonding in $KCu(CN)_2$ solid is developed and justified on the basis of these observed experimental facts.

Calculations

The model developed has three primary features: (1) The Cu atom uses a set of three sp^2 -hybrid orbitals to form three σ bonds to the neighboring CN groups. The experimental bonds are distorted from a symmetrical triangle to conform with the observed bond angles. This bonding assumption is justified by the near-trigonal arrangement of CN groups about the Cu atom in the solid and is further supported by the possibility of the $Cu(CN)_2^-$ being nonlinear in solution. (2) The Cu-C bonds have a significant amount of double bond character of a $d-\pi^*$ type, where elec-

(9) P. Niggli, *Z. Krist.*, **57**, 253 (1922).

(10) C. B. Knobler, *ibid.*, **111**, 385 (1959).

(11) I. D. Brown and J. D. Dunitz, *Acta Cryst.*, **14**, 480 (1961).

(12) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., pp 171-172.

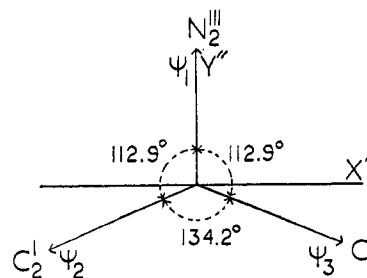


Figure 3.—Axis system for representation of σ hybrid orbitals.

trons are donated from the filled Cu d orbitals to the empty π^* antibonding orbital of the CN group. (3) The Cu-N bond has an appreciable amount of either incomplete orbital overlap or ionic character, or a combination of the two.

A set of three sp^2 -hybrid orbitals is developed for the Cu atom using as a basis hydrogenlike atomic orbitals (AO). The orientation of these hybrids relative to a reference axis system, x'', y'', z'' , which one should remember is practically coincidental with the EFG principal axis system, is shown in Figure 3. Using the bond angles shown in Figure 3 and the angular portions of the wave functions,¹³ the coefficients for the hybrid orbitals were determined by maximizing ψ_2 at 112.9° and using the conventional orthogonality and normalization relationships. The three hybrid orbitals used are

$$\begin{aligned}\psi_1 &= 0.404s + 0.915p_x \\ \psi_2 &= 0.647s - 0.286p_x + 0.707p_y \\ \psi_3 &= 0.647s - 0.286p_x - 0.707p_y\end{aligned}\quad (1)$$

The contribution to the EFG tensor components due to a single electron in each of the hybrid orbitals, ψ_n , is found by using the conventional average value expression

$$q_{rs}(\psi_n) = \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_n^* [q_{rs}]_{op} \psi_n r^2 \sin \theta \, dr d\theta d\varphi \quad (2)$$

where $n = 1, 2, 3$, $rs = XX, XY, XZ, YY, YZ, ZZ$, and the operators, $[q_{rs}]_{op}$, are given in Table IV. It is noted that these components are products of angular and radial functions, the latter of which are common to all AO's involved in the calculations, since the $4s$ orbitals will not contribute to the EFG because of their spherical symmetry. The radial part is given by

$$e \left\langle \frac{1}{r^3} \right\rangle = \frac{2Z_e^3 e}{n^3 a_0^3 l(l+1)(2l+1)} \quad (3)$$

where n is the principal quantum number, l is the orbital quantum number, Z_e is the effective atomic number, e is the electron charge, and a_0 is the Bohr radius.

TABLE IV

OPERATORS FOR EFG TENSOR COMPONENTS

$$\begin{aligned}q_{XX} &= (e/r^3)(3 \sin^2 \theta \cos^2 \varphi - 1) & q_{YY} &= (e/r^3)(3 \sin^2 \theta \sin^2 \varphi - 1) \\ q_{XY} &= (e/r^3)(3 \sin^2 \theta \cos \varphi \sin \varphi) & q_{YZ} &= (e/r^3)(3 \sin \theta \cos \theta \sin \varphi) \\ q_{XZ} &= (e/r^3)(3 \sin \theta \cos \theta \cos \varphi) & q_{ZZ} &= (e/r^3)(3 \cos^2 \theta - 1)\end{aligned}$$

(13) W. Kauzmann, "Quantum Chemistry," Academic Press, Inc., New York, N. Y., 1957, p 731.

Using the rules given by Kauzmann¹⁴ for calculation of screening constants, the effective atomic number of Cu⁺ is 3.7. For 4p electrons the radial contribution, $e(1/r)^3 = 8.56 \times 10^{14}$ esu cm⁻³. This value, combined with the angular contributions listed in Table V, gives the contributions from each hybrid as listed in Table V also. Since the axis system chosen for the

TABLE V
EFG TENSOR COMPONENTS^a

Contribution of a Single Electron in a Single Atomic Orbital

Atomic orbital	EFG tensor component $\times 10^{-14}$ esu cm ⁻³		
	q_{XX}	q_{YY}	q_{ZZ}
4p _x	-6.84	3.42	3.42
4p _y	3.42	-6.84	3.42
4p _z	3.42	3.42	-6.84
3d _{z²}	1.16	1.16	-2.32
3d _{x²-y²}	-1.16	-1.16	2.32
3d _{xy}	-1.16	-1.16	2.32
3d _{xz}	-1.16	2.32	-1.16
3d _{yz}	2.32	-1.16	-1.16

Contribution of a Single Electron or Hole in a Hybrid Orbital

Hybrid orbital	q_{XX}	q_{YY}	q_{ZZ}
ψ_1	-5.73	2.86	2.86
ψ_2	1.15	-3.14	1.99
ψ_3	1.15	-3.14	1.99
ψ^{π}_1	1.16	-0.58	-0.58
ψ^{π}_2	1.16	-0.58	-0.58

^a Total contribution of hybrid orbitals: q_{XX} , -1.11; q_{YY} , -4.58; q_{ZZ} , 5.68. Total contribution of hybrid orbitals with an arbitrary contribution, α , of ψ_1 : q_{XX} , $4.06 - 5.73\alpha$; q_{YY} , $-5.92 + 2.86\alpha$; q_{ZZ} , $1.86 + 2.86\alpha$.

hybrid orbital representation coincides with the principal EFG axis system all cross terms, q_{XY} , q_{XZ} , and q_{YZ} , are zero.

The 3d AO's which can participate in d- π^* bonding are determined by group theory using the fact that the Cu atom site has C_{2v} symmetry. It is found that either the 3d_{xy}, 3d_{yz} pair or the 3d_{x²-y²}, 3d_{xz} pair is available for π -bond formation. The latter pair is used to form a pair of hybrid π orbitals directed along the Cu-C bonds and given by

$$\psi^{\pi}_1 = 0.707d_{x^2-y^2} + 0.707d_{xz}$$

$$\psi^{\pi}_2 = 0.707d_{x^2-y^2} - 0.707d_{xz}$$

The first pair is not considered since these give calculated values of q_{XX} and q_{YY} which are reversed in relative magnitude compared to the experimental values. Using eq 2 and 3 the contributions to the EFG tensor components due to a single electron in each 3d orbital and due to a hole in each of the two π -hybrid orbitals are calculated and given in Table V.

Discussion

The value of the asymmetry parameter, $\eta = 0.61$, for the total EFG tensor components based on the three σ orbitals and two π orbitals is lower than the experimental value of $\eta = 0.78$. There are three primary factors which influence the asymmetry param-

eter: (1) the introduction of ionic character into the σ bonds, (2) the decreased overlap of the copper and nitrogen orbitals due to the deviation of the bonding angle from 180°, (3) the π bonding involves less than one electron per bond. A reduction in the amount of π bonding will reduce the calculated asymmetry parameter still further, so this is good evidence that there is one electron donated from the copper atom to each π bond to adjacent carbon atoms. Introduction of ionic character or reduced overlap into the σ bonds not only will increase the asymmetry parameter but also will decrease the magnitude of q_{ZZ} , a factor which is also desirable as will be discussed later.

Using the electronegativity value given by Jørgensen¹⁵ for CN⁻ in coordination compounds, $X_{CN} = 2.8$, and the Pauling value for copper, $X_{Cu} = 1.7$, the ionic character of the Cu-CN bonds is estimated to be $(X_{CN} - X_{Cu})/(X_{CN} + X_{Cu}) = 0.24$. Using this value for ψ_2 and ψ_3 and letting α be the fractional contribution of an electron in ψ_1 , the EFG tensor components are calculated and given as the last entry in Table V. Using the experimental value of $\eta = 0.78$ one solves

$$\frac{|q_{XX}| - |q_{YY}|}{|q_{ZZ}|} = \frac{(4.06 - 5.73\alpha) - (-5.92 + 2.86\alpha)}{(1.86 + 2.86\alpha)} = 0.78 \quad (4)$$

to get $\alpha = 0.78$. This value is reasonable in view of the incomplete overlap as indicated by the Cu^IN₂^{III}C₂^{III} bond angle being 139° and the difference in electronegativity of the Cu atom and the CN group. This gives a calculated value for the Z component of the EFG tensor, $(q_{ZZ})_{\text{calcd}} = 4.09 \times 10^{14}$ esu cm⁻³.

The calculated value for the Z component is related to the experimental value by

$$(q_{ZZ})_{\text{exptl}} = (1 - \gamma_{\infty})(q_{ZZ})_{\text{calcd}}$$

where γ_{∞} is the Sternheimer polarization factor.¹⁶ This factor allows for the polarization of the inner shell electrons by the quadrupole moment of the nucleus. Calculations of γ_{∞} for Cu⁺ have given values varying from -8.7 to -17.0.¹⁶⁻¹⁸ Using the calculated value, $(q_{ZZ})_{\text{calcd}} = 4.09 \times 10^{14}$ esu cm⁻³, and the experimental value, $(q_{ZZ})_{\text{exptl}} = 5.4 \times 10^{15}$ esu cm⁻³, the Sternheimer factor is found to be $\gamma_{\infty} = -12.2$. Considering that the KCu(CN)₂ system does not represent an ionic lattice, such as Cu₂O where q_{ZZ} can be calculated exactly based on an ionic model¹⁷ and $\gamma_{\infty} = -16.5$, this represents very good agreement.

There are four other factors which were investigated and their contributions shown to be sufficiently small to neglect. (1) The presence of the K⁺ ions will contribute to the EFG at the Cu nuclei. Using the crystal structure data to get the coordinates of the eight nearest

(15) C. K. Jørgensen, "Orbitals in Atoms and Molecules," Academic Press Inc., New York, N. Y., 1962, p 95.

(16) H. M. Foley, R. M. Sternheimer, and D. Tycho, *Phys. Rev.*, **93**, 734 (1954).

(17) E. G. Wikner and T. P. Das, *ibid.*, **109**, 360 (1958).

(18) R. M. Sternheimer, *ibid.*, **130**, 1423 (1963).

(14) Reference 13, p 333.

neighbor K^+ ions to Cu^I the contribution to q_{zz} is calculated to be 0.05×10^{14} esu cm^{-3} . This is less than 1% of $(q_{zz})_{calcd.}$ (2) While π bonding between the Cu^I atom and the N_2^{III} atom is unfavorable from the standpoint of the bond angle the effect of its presence was examined. The addition of π bonding to the $Cu^I-N_2^{III}$ bond will sharply lower the asymmetry parameter and hence is considered to be absent. (3) There is the possibility that the amount of π bonding between the Cu^I atom and the carbon atoms is less than that due to the contribution of one electron to each ligand bond. A reduction of the π bonding not only decreases the asymmetry parameter as was indicated earlier but also increases $(q_{zz})_{calcd.}$ Both of these changes are in opposition to experimental findings and lead to decreased agreement with known Sternheimer factors. (4) If one considers the absence of any π bonding, then it is necessary to decrease the contribution, α , of the ψ_1 orbital to the EFG tensor to 0.38 to have agreement between the experimental and calculated asymmetry

parameters. This would also require a value of the Sternheimer factor of -16.1 , which is close to that observed for a completely ionic Cu^+ species. In view of the observed $Cu^I-N_2^{III}$ bond distance it is very unlikely that both incomplete overlap and ionic character together could cause that much electron depletion from the ψ_1 orbital.

Summary

The EFG tensor components and asymmetry parameter as calculated on the basis of three sp^2 -hybrid σ bonds and two $d-\pi^*$ bonds from the Cu atom to the three nearest CN groups are in good agreement with experimental values. Consideration of all factors indicates that there must be a large amount of π bonding to lead to this agreement. While the total contribution of the $Cu^I-N_2^{III}$ bonding orbital to the EFG tensor can be determined, it is not possible to say how much is due either to ionic character or to incomplete overlap alone.

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The Rate of Aquation of the Sulfito Ligands in $Co(CN)_4(SO_3)_2^{5-}$ and $Co(CN)_5(SO_3)^{4-}$

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The rates of water displacement of a single SO_3^{2-} ligand in $Co(CN)_5(SO_3)^{4-}$ and in $Co(CN)_4(SO_3)_2^{5-}$ were measured at 25°. Values of the acidity constants of $HCo(CN)_5(SO_3)^{3-}$ and $HCo(CN)_4(SO_3)_2^{4-}$ were obtained using conventional acid-base titration and spectrophotometric techniques. The kinetic studies yield values of the acidity quotients of $HCo(CN)_4(SO_3)_2^{4-}$ and $H_2Co(CN)_4(SO_3)_2^{3-}$. Infrared and Raman studies provide evidence that $Co(CN)_4(SO_3)_2^{5-}$ has a *trans* configuration.

Introduction

In the present work we are mainly concerned with the rate of water displacement of the SO_3^{2-} ligands in $Co(CN)_4(SO_3)_2^{5-}$ and $Co(CN)_5(SO_3)^{4-}$. However, acidity quotients are also reported for $HCo(CN)_4(SO_3)_2^{4-}$ and $HCo(CN)_5(SO_3)^{3-}$. In addition, infrared and Raman measurements were made to determine the configuration and nature of the bonding of the SO_3^{2-} ligands.

It has been found that the rate of aquation of the first SO_3^{2-} ligand in $Co(CN)_4(SO_3)_2^{5-}$ is very much greater than that of the SO_3^{2-} ligand present in either $Co(CN)_4(SO_3)_2^{5-}$ or $Co(CN)_5(SO_3)^{4-}$. This observation combined with our unpublished studies of the rate of ligation of $Co(CN)_4(SO_3)_2^{5-}$ strongly suggests that the rapid aquation of $Co(CN)_5(SO_3)^{4-}$ represents an unusually large *trans* activation by SO_3^{2-} ,

a suggestion which has been made by others to explain the steric course of certain preparative reactions.^{3,4} The infrared and Raman measurements support the assumption that $Co(CN)_4(SO_3)_2^{5-}$ has a *trans* configuration.

Experimental Section

Reagents.—All inorganic chemicals were of reagent grade. Buffer solutions were prepared using Baker and Adamson reagent grade potassium acid phthalate or acetic acid, or Eastman Kodak phenylacetic acid. Stock solutions of $NaClO_4$ and $LiClO_4$, prepared by dissolving Na_2CO_3 or Li_2CO_3 in $HClO_4$ solutions, were used to adjust the ionic strength.

Preparation of $Na_5[Co(CN)_4(SO_3)_2] \cdot 3H_2O$.—The complex was prepared by the method of Rây and Chackrabarty⁵ in which an SO_2 -saturated cobalt(II) acetate solution is added slowly to a well-stirred solution of concentrated $NaCN$ at 0°. The solid must be recrystallized to remove at least two known impurities,

(3) J. C. Bailar and D. F. Peppard, *J. Am. Chem. Soc.*, **62**, 105 (1940).

(4) A. V. Babaeva and I. B. Boranovskii, *Russ. J. Inorg. Chem.*, **7**, 404 (1962).

(5) P. R. Rây and S. Ch. Chackrabarty, *Z. Anorg. Allgem. Chem.*, **211**, 173 (1933).

(1) This work was supported by the Atomic Energy Commission.

(2) Taken in part from the M.S. thesis of H. H. Chen submitted in Dec. 1965.