

The Use of Electron Population Parameters to Distinguish Between Carbon and Nitrogen in Cyanide Complexes*

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Valence-electron population parameters have been applied to a number of complexes of copper(I) cyanide for the purpose of distinguishing between carbon and nitrogen atoms in the cyanide groups. The method appears to be more objective than relying on thermal parameters and bond lengths and angles.

In this laboratory we have determined the crystal structures of a number of complex copper (I) cyanides. In many cases it has been difficult to identify the atoms in cyanide groups, particularly if both ends of the group are bonded in a linear bridge. Thermal parameters, bond lengths and bond angles have been the criteria on which carbon and nitrogen atoms were distinguished. In a recent paper on the structure of $\text{Cu}_3(\text{en})_2(\text{CN})_4 \cdot \text{H}_2\text{O}$ (Williams, Larson & Cromer, 1972), however, a more direct approach was used. Valence-electron population parameters, p_v , were assigned by means of Stewart's (1969, 1970) generalized scattering factors and L -shell projection method. The method had first been tested on the compound $\text{CuCN} \cdot 4$ -cyanopyridine (Cromer & Larson, 1972), because this compound has an unambiguously oriented cyano group attached to the ring and the cyanide ion had been oriented with reasonable certainty by conventional methods. We have now re-examined most of the cyanide compounds we studied earlier, and this note reports the results.

If ordinary scattering factors are used and for example, an atom is identified as nitrogen when it is really carbon, the thermal parameters become anomalously high. If the L -shell is separated, however, the thermal parameters tend to be normal, whichever way the atoms are identified, but the p_v parameters show the difference directly. The scattering factors used for carbon and nitrogen in testing the method on these compounds were computed from Hartree-Fock (HF) $1s^2$ cores and molecular optimized Slater type orbital (STO) L -shells with ζ 's given by Hehre, Stewart & Pople (1969). Averaged carbon and nitrogen core and valence scattering factors were also used. In some cases the scattering factor of copper was also separated and the HF core (Ar configuration) was used along with the HF $3d$ orbital for the valence electrons. Regardless of whether the carbon, nitrogen, or averaged form factors were used for either carbon or ni-

trogen, the identity of an atom was clear from the relative values of p_v at the atom site.

Some results from $\text{CuCN} \cdot 4$ -cyanopyridine (Cromer & Larson, 1972) are shown in Table 1. The distinction between carbon and nitrogen is clear in all cases. No constraints were placed on any of the parameters.

Table 1. *Valence electron populations in $\text{CuCN} \cdot 4$ -cyanopyridine*

The cyanide ion is C(1)-N(1) and the cyano group on the ring is C(7)-N(3). Scattering factors were f_c and f_n .

Correct atom site	Correct orientation	Valence electrons at atom site		
		C(1), N(1) reversed	C(7), N(3) reversed	Both reversed
C(1)	4.07	3.39	4.15	3.44
N(1)	5.00	5.80	5.05	5.87
C(7)	3.59	3.64	3.00	3.04
N(3)	5.06	5.10	5.76	5.80

Table 2 shows some results from a refinement of $\text{CuCN} \cdot \text{pyridazine}$ (Cromer & Larson, 1972). Population parameters were applied to all atoms. When all parameters were allowed to vary, the total number of valence electrons, which should be 50 in the formula unit, became quite large (71.9 electrons), but normalized or relative values distinguished clearly between the atoms. When the valence electrons of the copper atoms were held fixed at 11.0, the total number of electrons became 50.3. The correct form factors were used for the ring atoms but averaged carbon and nitro-

Table 2. *Valence electron populations for the cyanide groups in $\text{CuCN} \cdot \text{pyridazine}$*

Scattering factors for both carbon and nitrogen were $(f_c + f_n)/2$. The copper valence electrons were held fixed at 11.0.

Valence electrons at site	
C(1)	4.0 (3)
N(1)	5.7 (2)
C(2)	3.5 (2)
N(2)	5.4 (2)

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gen form factors were used for the cyanide groups. The ring atoms were also clearly identified.

Table 3 shows the results for $K_3Cu(CN)_4$ (Roof, Larson & Cromer, 1968). In this calculation a neutral potassium atom was used and the copper atom valence electrons were held fixed at 11.0. The values listed in the table have been normalized by a factor of 1.14 so that 47 valence electrons are associated with the $Cu(CN)_4$ group.

Table 3. *Valence electron populations for the cyanide groups in $K_3Cu(CN)_4$*

Scattering factors for both carbon and nitrogen were $(f_C + f_N)/2$. Values given have been normalized.

	Valence electrons at site
Cu	12.5
C(1)	3.2 (5)
N(1)	5.0 (6)
C(2)	2.8 (3)
N(2)	5.9 (3)

The results for $KCu_2(CN)_3 \cdot H_2O$ (Cromer & Larson, 1962) are shown in Table 4. In this calculation hydrogen was omitted, a neutral potassium scattering factor was used, and p_v was allowed to vary for copper, carbon, nitrogen and oxygen. The values have been normalized by a factor of 1.06 to give 55 valence electrons. Electron densities from Table 2 of Cromer & Larson (1962) are given for comparison purposes.

Table 4. *Valence electron populations in $KCu_2(CN)_3(CN)_3 \cdot H_2O$*

Scattering factors for both carbon and nitrogen were $(f_C + f_N)/2$. Values given have been normalized.

	Valence electrons at site	Electron density
Cu(1)	10.6 (3)	54.5
Cu(2)	10.5 (3)	58.3
C(1)	3.6 (3)	9.6
C(2)	4.0 (3)	9.9
C(3)	4.1 (3)	10.9
N(1)	5.3 (3)	9.9
N(2)	4.9 (3)	11.6
N(3)	5.2 (3)	11.3
O	6.8 (2)	11.1

The orientation of the cyanide group in $CuCN \cdot NH_3$ (Cromer, Larson & Roof, 1965) is somewhat ambiguous. On the basis of thermal parameters and R values, orientation II was favored and assumed to be correct. This orientation resulted in a linear Cu–N–C grouping rather than the usual Cu–C–N linear arrangement. The present calculations give further support to the selection made in the original paper. The results are shown in Table 5. The valence electrons of copper were held constant at 11.0 and the values shown have been multiplied by 0.961 to normalize to 25 valence electrons (the hydrogen atoms were omitted). The number of electrons associated with the ammonia nitrogen is

somewhat large, perhaps reflecting some contribution by the hydrogen atoms.

Table 5. *Valence electron populations in $CuCN \cdot NH_3$*

Scattering factors for both atoms in the cyanide group were $(f_C + f_N)/2$. Values given have been normalized.

	Valence electrons at site
Cu	10.6
C	3.6 (2)
N	4.6 (2)
NH_3	6.2 (2)

The compound $Cu_3(CN)_4(NH_3)_3$ (Williams, Cromer & Larson, 1971) is interesting because it has both Cu(I) and Cu(II) ions. Two of the cyanide groups are disordered by symmetry and some of the ammonia sites are only partly occupied. Table 6 shows the results of the electron population analysis. The Cu(1) site, which is occupied by the Cu(I) ion, was held fixed at 11.0 valence electrons. It is interesting, although probably fortuitous, that the Cu(II) ion, in the Cu(2) site has nearly one less valence electron than does the Cu(I). No population parameter was applied to the ammonia sites. The values in Table 6 have not been normalized.

Table 6. *Valence electron populations in $Cu_3(CN)_4(NH_3)_3$*

The scattering factors at the carbon and nitrogen sites were f_C and f_N respectively, and $(f_C + f_N)/2$ at the site of the disordered cyanide groups $D(1)$ and $D(2)$.

	Valence electrons at site
Cu(1)	11.0
Cu(2)	10.1 (2)
C	3.8 (2)
N	5.1 (2)
$D(1)$	4.5 (1)
$D(2)$	4.7 (1)

Table 7. *Valence electron populations in $Cu_3(en)_2(CN)_4 \cdot H_2O$*

Scattering factors used for the cyanide groups, C(1)–C(4) and N(1)–N(4) were $(f_C + f_N)/2$, and for the other carbon and nitrogen atoms, which are in the ethylenediamine groups, were f_C and f_N . Hydrogen atoms were omitted. Values given have not been normalized.

	Valence electrons at site		Valence electrons at site
Cu(1)	11.0	C(5)	4.1 (2)
Cu(2)	11.0	C(6)	3.9 (2)
Cu(3)	11.0	C(7)	4.2 (2)
C(1)	4.0 (2)	C(8)	5.3 (3)
C(2)	3.6 (2)	N(5)	5.0 (1)
C(3)	3.7 (1)	N(6)	5.0 (1)
C(4)	2.8 (2)	N(7)	5.3 (1)
N(1)	4.6 (2)	N(8)	4.8 (1)
N(2)	4.5 (2)	O	5.9 (2)
N(3)	4.4 (1)		
N(4)	4.5 (2)		

Finally, it was particularly difficult to determine the orientations of the cyanide groups in $\text{Cu}_3(\text{en})_2(\text{CN})_4 \cdot \text{H}_2\text{O}$ (Williams, Larson & Cromer, 1972) because all of the groups formed linear bridges between Cu(I) ions and there was pseudosymmetry that might have permitted disorder. The results are shown in Table 7. The copper atoms were held fixed at 11.0 valence electrons. The only anomaly is C(8), in an ethylenediamine group, which appears to have too many electrons.

The application of a population parameter to the valence electrons of an atom appears to be an objective method for assigning identities to atoms in chemically ambiguous or initially unknown molecular structures. The method also requires only a single least-squares run as opposed to two or more in which atom identities are interchanged.

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Polymorphisme du *p*-Chlorophénol. I. Structure Cristalline et Morphologie de la Forme Stable

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The phenomenon of polymorphism has been shown for *p*-chlorophenol. The α modification is monoclinic with unit-cell dimensions: $a = 8.840$, $b = 15.723$, $c = 8.788$ Å, $\beta = 92.63^\circ$. The space group is $P2_1/c$ with 8 molecules in the unit cell. The intensities were collected on an automatic three-circle diffractometer. Anisotropic block-diagonal least-squares refinement gave an R index of 0.067 for 1385 independent non-zero F values. The hydrogen bonding forms two chains in the unit cell, both parallel to the c axis.

Des études récentes de spectroscopie infrarouge et de résonance quadripolaire nucléaire sur les *p*-halogéno-phénols (Babushkin, Babushkina, Orlova, Sperantova & Semin, 1969) montrent l'existence de deux formes cristallines pour ces composés et en particulier pour le *p*-chlorophénol: $\text{ClC}_6\text{H}_4\text{OH}$. Des cristaux de la forme stable (que nous appellerons forme α) ont été obtenus par évaporation de solutions saturées avec le benzène ou l'éther de pétrole. Ils se présentent sous forme de plaquettes losangiques. La forme métastable (forme β) cristallise en aiguilles allongées suivant l'axe a (Perrin & Michel, 1971).

Faciès des cristaux

Les plaquettes obtenues en solution ont été utilisées comme germes pour la préparation de gros monocristaux en bain fondu. La croissance a été réalisée en boîte à gants car ces composés sont très hygroscopiques. Les cristaux obtenus d'un volume de 1 à 2 cm³ ont le faciès suivant: une série de faces en zone pa-

rallèles à l'axe c sont toujours présentes; les faces $\{0\bar{1}1\}$ et $\{021\}$ sont très développées tandis que la face $\{111\}$ n'apparaît que rarement. La Fig. 1 représente un tel cristal et sa projection stéréographique.

Données expérimentales

Les mesures nécessaires à la détermination de la structure ont été faites sur un monocristal enfermé dans un tube en verre de Lindemann de 0,2 mm de diamètre; 1896 réflexions indépendantes ont été mesurées avec le rayonnement du cuivre sur un diffractomètre automatique Siemens mis à notre disposition par le Laboratoire de Cristallographie de Bordeaux.

Les paramètres sont les suivants:

$$\begin{aligned} a &= 8,841 \pm 0,003 \text{ \AA} \\ b &= 15,726 \pm 0,002 \\ c &= 8,790 \pm 0,0015 \\ \beta &= 92,61^\circ \pm 0,02 \end{aligned}$$