

# Electronic Structure and Absorption Spectrum of Copper(II)-bis(2-imine-4-amine methylpentane) Nitrate

T. OBERT

*Institute of Inorganic Chemistry, Slovak Academy of Sciences,  
Bratislava 9*

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In the present work the electronic structure of copper(II)-bis(2-imine-4-amine methylpentane) nitrate  $\text{Cu}(\text{C}_6\text{N}_2\text{H}_{14})_2(\text{NO}_3)_2$  was calculated by the SCCM MO method and the characteristics of the absorption spectrum of the aqueous solution of this substance was determined with the aid of a qualitative configuration interaction.

## Experimental

X-ray analysis of the compound in question was reported by *Hanic et al.* [1] (Fig. 1). The complex shows a centre of inversion, the local symmetry in the crystal being  $C_i$ .

In order to facilitate the calculations we have limited our discussion to atoms the distance of which from the central atom is smaller than 3 Å. Thus we have considered only those ligand atoms which are enumerated in Fig. 1. Their spherical coordinates are listed in Table 1. A preliminary discussion has shown that with this simplification a fair agreement with the experiment can be obtained.

## Theoretical

The electronic structure of the complex was calculated with the SCCM MO method [2, 3]. *Mulliken* population analysis [4] was applied in this method and the procedure was performed until a self-consistency of the charge and configuration of the central ion was attained. A slightly modified Johansen's programme (transcribed into ALGOL-4) was used for this purpose. The detailed assumptions were as follows:

a) *Coulomb integrals for the central atom*  $\text{Cu}^{2+}$ . These integrals were approximated by the negative ionization potential of the appropriate valence state (VOIP)

Table 1

Atom	$r_i$ [Å]	$\vartheta_i$ [°]	$\varphi_i$ [°]
1	2.01	90	0
2	2.01	90	180
3	1.98	90	92
4	1.98	90	272
5	2.75	1.08	0.58
6	2.75	178.92	180.58
7	2.95	94.29	74.79
8	2.95	85.71	254.79

$$\text{VOIP}_{\text{C.I.}} = Aq^2 + Bq + C$$

where  $q$  is the net charge of the central ion and  $A$ ,  $B$ , and  $C$  are constants [5].

b) *Coulomb integrals for ligands.* Calculating the Coulomb integrals we have made the following choice of the ligand orbitals.

For nitrogen atoms in positions 1 and 2 the hybridization  $sp^3$  was assumed with 5 electrons in the valence shell. The lone pair orbitals  $\sigma_1$  and  $\sigma_2$  were thus of the following form

$$\sigma_1 = \sigma_2 = \frac{1}{2} s(\text{N}) + \frac{\sqrt{3}}{2} p_\sigma(\text{N}).$$

In the case of nitrogen atoms in the position 3 and 4, on the other hand, a hybridization  $sp^2$  was assumed with 4 electrons in these orbitals. The remaining  $2p$ -electron was reserved for the  $\pi$ -bond with the carbon atom. We assumed thus the following form of the lone pair orbitals  $\sigma_3$  and  $\sigma_4$

$$\sigma_3 = \sigma_4 = \frac{1}{\sqrt{3}} s(\text{N}) + \frac{\sqrt{2}}{\sqrt{3}} p_\sigma(\text{N}).$$

Oxygen atoms in positions 5 and 6 were represented by the significant part of the highest occupied molecular orbital of  $\text{NO}_3^-$  [6]

$$\sigma_5 = \sigma_6 = 0.230252 p_6(\text{O}) +$$

In the calculation we included also the  $\pi$ -orbitals of the aggregates  $\text{>C=N<}$  (both bonding and antibonding, to be described later), the  $\pi$ -orbitals being resolved into the  $\pi_\sigma$ - and  $\pi_\varphi$ -components (Fig. 2).

VOIP for the nitrogen atoms in positions 1 and 2 was calculated according to eq. (1)

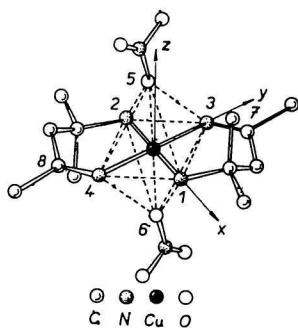


Fig. 1. Structure of the complex  $\text{Cu}(\text{C}_6\text{N}_2\text{H}_{14})_2(\text{NO}_3)_2$ .

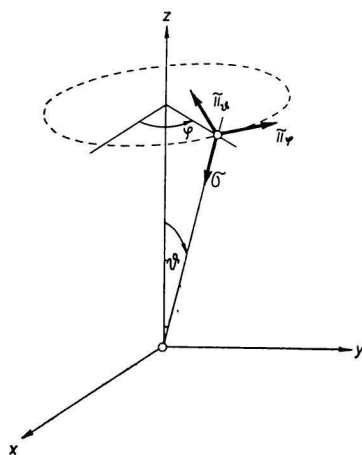


Fig. 2. Resolving of  $\pi$ -orbitals into  $\pi_\sigma$ - and  $\pi_\varphi$ -components.

$$\text{VOIP}_\sigma(sp^3) = \frac{1}{4} \text{VOIP}(s) + \frac{3}{4} \text{VOIP}_\sigma(p). \quad (1)$$

In order to find  $\text{VOIP}(s)$  and  $\text{VOIP}_\sigma(p)$  let us decompose the average configuration of the nitrogen atom  $s^{5/4} p^{15/4}$

$$\{s^{5/4} p^{15/4}\} = \frac{1}{4} \{s^2 p^3\} + \frac{3}{4} \{sp^4\}.$$

Thus, following the *Ballhausen* and *Gray* prescription for the central atom [3]

$$\begin{aligned} \text{VOIP}(s) &= \frac{1}{4} \text{VOIP}_s(s^2 p^3) + \frac{3}{4} \text{VOIP}_s(sp^4), \\ \text{VOIP}_\sigma(p) &= \frac{1}{4} \text{VOIP}_p(s^2 p^2) + \frac{3}{4} \text{VOIP}_p(sp^4). \end{aligned}$$

$\text{VOIP}_\sigma(p)$  for  $\sigma$ -bonds is according to [7] larger by 10 kK than  $\text{VOIP}_\pi(p)$  for  $\pi$ -bonds. Therefore

$$\text{VOIP}_\sigma(p) = \text{VOIP}_\pi(p) + 10.$$

Substituting the numerical values reported by *Basch*, *Viste* and *Gray* [8] into these equations we find that  $\text{VOIP}_\sigma(sp^3) = 154.18$  kK.

Following a similar procedure we find also the  $\text{VOIP}(sp)$  value, *i.e.* the  $\text{VOIP}$  of nitrogen atoms in positions 3 and 4:  $\text{VOIP}_\sigma(sp^2) = 160.95$  kK.

The  $\text{VOIP}_\sigma(\text{NO}_3^-)$ , *i.e.* of the highest occupied molecular orbital was taken over from ref. [6]. ( $\text{VOIP}_\sigma(\text{NO}_3^-) = 67.35$  kK.)

$\text{VOIP}$  values of bonding and antibonding  $\pi$ -orbitals of the aggregates  $\text{>C=N<}$  were obtained from the secular equation of the extended Hückel method

$$\begin{vmatrix} \text{H}_{\text{NN}} - \varepsilon & \text{H}_{\text{CN}} - \text{S}_{\text{CN}} \\ \text{H}_{\text{CN}} - \text{S}_{\text{CN}} & \text{H}_{\text{CC}} - \varepsilon \end{vmatrix} = 0 \quad (2)$$

where  $\text{H}_{\text{NN}} = -\text{VOIP}_\pi(s^{4/3} p^{18/3} + p) = -121.73$  kK and  $\text{H}_{\text{CC}} = -\text{VOIP}_\pi(sp^2 = p) = -86.9$  kK, as calculated for the average configuration in the way described already. The resonance integral  $\text{H}_{\text{CN}}$  was calculated from the Cusachs formula.  $\text{S}_{\text{CN}}$  is the overlap integral between the  $2p_x$ -orbitals of atoms C and N. Solving equation (2) we get the two eigenvalues  $\varepsilon_b$  and  $\varepsilon_a$  of the bonding and antibonding  $\pi$ -orbitals. Thus

$$\text{VOIP}_\pi(\text{C=N}) = -\varepsilon_b = -127.29 \text{ kK},$$

$$\text{VOIP}_{\pi^*}(\text{C=N}) = -\varepsilon_a = -66.40 \text{ kK}.$$

The respective  $\pi$ -functions are as follows

$$\begin{aligned} \pi_{3\phi} &= 0.847285 p_{3\phi}(\text{N}) + 0.315130 p_{7\phi}(\text{C}) \\ \pi_{3\psi} &= -0.902458 p_{3\psi}(\text{N}) - 0.317276 p_{7\psi}(\text{C}) \\ \pi_{3\phi}^* &= -0.655126 p_{3\phi}(\text{N}) + 1.012365 p_{7\phi}(\text{C}) \\ \pi_{3\psi}^* &= 0.608518 p_{3\psi}(\text{N}) - 0.888866 p_{7\psi}(\text{C}) \\ \pi_{4\phi} &= 0.847285 p_{4\phi}(\text{N}) + 0.315130 p_{8\phi}(\text{C}) \\ \pi_{4\psi} &= 0.902458 p_{4\psi}(\text{N}) + 0.317276 p_{8\psi}(\text{C}) \\ \pi_{4\phi}^* &= -0.655126 p_{4\phi}(\text{N}) + 1.012365 p_{8\phi}(\text{C}) \\ \pi_{4\psi}^* &= -0.608518 p_{4\psi}(\text{N}) + 0.888866 p_{8\psi}(\text{C}) \end{aligned}$$

c) *Resonance integrals* were calculated from the Cusachs formula

$$H_{ij} = (2 - |S_{ij}|) \frac{H_{ii} + H_{jj}}{2} G_{ij}$$

where  $S_{ij}$  and  $G_{ij}$  are atomic and group overlap integrals, respectively, and  $H_{ii}$ ,  $H_{jj}$  are the diagonal elements.

d) *Standard overlap integrals* over linear combination of Slater-type orbitals were calculated with the use of the programme kindly supplied by Dr. H. Johansen. Atomic valence orbitals of Cu were taken from ref. [9] and those of N, O and C atoms from ref. [10].

e) *Group overlap integrals* were reduced to standard overlap integrals in accordance with the formulae reported in ref. [11, 12] a programme being written for these integrals in ALGOL-4.

### Electronic structure and absorption spectrum of the complex

The electronic structure of the complex obtained in these calculations is summarized in Table 2. In column 1 we give the calculated orbital energies in kK, in column 2 the contribution to the ground state configuration and the approximate character of the orbital, in brackets.

Table 2

Energy	Configurations
-185.60	$(1a_g)^2$ ; $(\sigma_{34} > \sigma_{12} > 4s)$
-172.04	$(2a_g)^2$ ; $(d_{x^2-y^2} > \sigma_{12})$
-163.89	$(1a_u)^2$ ; $(\sigma_{34})$
-159.34	$(2a_u)^2$ ; $(\sigma_{12} > \pi_{34\phi})$
-157.02	$(3a_g)^2$ ; $(d_{xy} > \pi_{34\phi})$
-156.82	$(4a_g)^2$ ; $(d_{yz} > \pi_{34\phi})$
-153.81	$(5a_g)^2$ ; $(d_{xz})$
-149.79	$(6a_g)^2$ ; $(d_z^2)$
-129.32	$(3a_u)^2$ ; $(\pi_{34\phi})$
-122.99	$(7a_g)^2$ ; $(\pi_{34\phi} > d_{yz})$
-122.61	$(4a_u)^2$ ; $(\pi_{34\phi} > \sigma_{12})$
-122.31	$(8a_g)^2$ ; $(\pi_{34\phi} > d_{xy})$
-99.48	$(9a_g)^1$ ; $(\sigma_{12} \sim d_{x^2-y^2} > \sigma_{34})$
-67.43	$(5a_u)^0$ ; $(\sigma_{56})$
-67.34	$(10a_g)^0$ ; $(\sigma_{56})$

Table 3

Orbital excitation	Transition	$E_{\text{calc}}$ [kK]	$E_{\text{obs}}$ [kK]
$8a_g \rightarrow 9a_g$	${}^2A_g \leftrightarrow {}^2A_g$	< 22.83	(c) } 17.8 (A)
$4a_u \rightarrow 9a_g$	${}^2A_g \rightarrow {}^2A_u$	< 23.13	(a) }
$7a_g \rightarrow 9a_g$	${}^2A_g \leftrightarrow {}^2A_g$	> 23.51	(d) }
$9a_g \rightarrow 5a_u$	${}^2A_g \rightarrow {}^2A_u$	> 32.05	(b) } 29.0 (B)
$9a_g \rightarrow 10a_g$	${}^2A_g \leftrightarrow {}^2A_g$	> 32.14	(e) }

It is seen from Table 2 that the ground state configuration of the complex is  $(1a_g)^2 (8a_g)^2 (9a_g)^1$ , with the ground state term  ${}^2A_g$ . In Table 3 we list possible excitations, the forbidden transitions denoting by  $(+\rightarrow)$  and the allowed ones by  $(-\rightarrow)$  [13]. We also compare the orbital excitation with the observed energies of transitions. The inequality signs indicate the shift expected qualitatively after a configuration interaction [14].

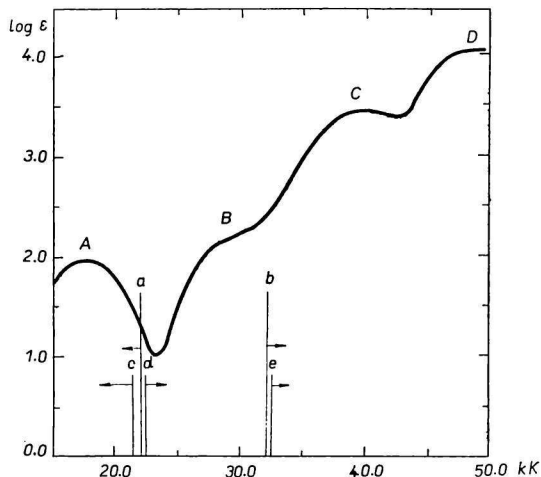


Fig. 3. Absorption spectrum of the complex  $\text{Cu}(\text{C}_6\text{N}_2\text{H}_{14})_2(\text{NO}_3)_2$ .

An attempt to interpret the spectrum of the  $\text{Cu}(\text{C}_6\text{N}_2\text{H}_{14})_2(\text{NO}_3)_2$  complex is given in Fig. 3. The intensities of calculated transitions are reproduced in arbitrary units, the allowed transitions taken as more intense than the forbidden ones. Arrows indicate the expected effect of the configuration interaction. As one can see it is tempting to assign the band A to the calculated transition a ( $4a_u \rightarrow 9a_g$ ), corresponding to a charge transfer of  $\pi$ -electrons of the CN groups to the central atom and the other ligands. Band B would thus correspond to the transition b ( $9a_g \rightarrow 5a_u$ ). In this transition there is a charge transfer expected from the nitrogen atom of the  $-\text{RNH}_2$  groups and of the central atom  $d$ -orbital to the nonbonding orbital of the  $\text{NO}_3^-$  group (a back donation). However, we cannot exclude other interpretations, like excitations of the c, d or e type (Fig. 3).

Bands C and D are internal transitions due to the ligands  $\text{NO}_3^-$ . Measurements of absorption spectra of aqueous solutions of  $\text{HNO}_3$ ,  $\text{NaNO}_3$ , and  $\text{KNO}_3$  are in good agreement with this assumption.

As we see the SCC MO method we have used yields a satisfactory characteristics of absorption spectrum of the complex.

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## References

1. Hanic F., Serátor M., *Chem. Zvesti* **18**, 572 (1964).
2. Ballhausen C. J., Gray H. B., *Inorg. Chem.* **1**, 111 (1962).
3. Ballhausen C. J., Gray H. B., *Molecular Orbital Theory*. Benjamin, New York, 1964.
4. Mulliken R. S., *J. Chem. Phys.* **23**, 1833 (1955).
5. Johansen H., Ballhausen C. J., *Mol. Phys.* **10**, 175 (1966).
6. McEwen K. L., *J. Chem. Phys.* **34**, 547 (1961).
7. Basch H., Viste A., Gray H. B., *J. Chem. Phys.* **44**, 10 (1966).
8. Basch H., Viste A., Gray H. B., *Theor. Chim. Acta* **3**, 458 (1965).
9. Synek M., *Phys. Rev.* **131**, 1572 (1963).
10. Clementi E., *Tables of Atomic Functions*, Suppl. IBM; *J. Res. Dev.* **9**, 2 (1965).
11. Gołębiewski A., *Acta Phys. Polon.* **23**, 243 (1963).
12. Obert T., Gołębiewski A., *Acta Phys. Polon.* **A40**, 97 (1971).
13. Herzberg G., *Molecular Spectra and Molecular Structure*, Vol. III. Van Nostrand, Toronto, 1967.
14. Gołębiewski A., Kowalski H., *Theor. Chim. Acta* **12**, 293 (1968).

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