

Saldarriaga & Clearfield 1986). The Al, P and two O atoms were clearly revealed in contour maps prepared at a contour interval of $0.1 e \text{ \AA}^{-3}$. These results indicate that a great deal of structural information can be obtained from fairly limited data even when the reflections are broadened or subject to a certain amount of error as a result of preferred orientation as layered compounds surely must be.

We gratefully acknowledge financial support of this study by the Regents of Texas A&M University through the commitment to Texas Program and the State of Texas through the Advanced Technology Program. We thank Professor G. Alberti and his coworkers at the University of Perugia for the crystals and Dr Nancy K. McGuire for collecting the data set using the synchrotron source. We also wish to thank Dr David Cox for assistance in obtaining the synchrotron data at the National Synchrotron Light Source at Brookhaven National Laboratory, which is supported by the United States Department of Energy, Division of Materials Sciences, and Division of Chemical Science. Travel to Perugia and consultation with colleagues at the University of Perugia was made possible through NATO Grant No. 870031 and the National Science Foundation US-Italy program through grant No. INT-8613467.

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X-ray Analysis of Wavefunctions by the Least-Squares Method Incorporating Orthonormality. II. Ground State of the Cu^{2+} Ion of Bis(1,5-diazacyclooctane)-copper(II) Nitrate in a Low-Symmetry Crystal Field

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(Received 25 February 1993; accepted 16 July 1993)

Abstract

Analysis of the d wavefunctions of Cu^{2+} in $[\text{Cu}(\text{daco})_2](\text{NO}_3)_2$ ($\text{daco} = 1,5\text{-diazacyclooctane}$) was carried out successfully using the least-squares method incorporating orthonormality. The Cu^{2+} ion is coordinated square planarly by four N atoms which form the C_4 crystal field. The deformation

density after refinement with spherical scattering factors showed the hole orbital of Cu^{2+} in the Cu-N_4 coordination plane. The deformation density in the plane perpendicular to the coordination plane could not be represented well without introducing κ parameters, assigned to each d orbital, which took into account the expansion and contraction of each d orbital. The difference densities after d -orbital analy-

sis revealed peaks due to anharmonic vibration of Cu^{2+} in the plane perpendicular to the coordination plane. Analysis of these peaks showed that they were well explained and it became clear that they were overlapped by dominantly large peaks due to expansion of the d orbitals. The role of the κ parameters in X-ray atomic orbital analysis is discussed in detail together with other technical details. Any unitary transformation of the atomic orbitals gives the same electron density if the basis functions of all the atomic orbitals are exactly the same. Different κ parameters for different d orbitals remove this ambiguity. Therefore, κ parameters assigned to each d orbital are essential for successful X-ray atomic orbital analysis.

Introduction

In the previous article [Tanaka, 1988; hereafter referred to as (A)] a method was described which permitted us to obtain molecular orbitals (MO) or atomic orbitals (AO) from the structure factors measured by X-ray diffraction methods. The first aim of the present article is to show how the method may be applied to the analysis of d orbitals in a low-symmetry crystal field, C_i , within the framework of crystal-field theory, which neglects the overlap densities between a metal and ligand orbitals.

We have analyzed d -electron densities measured using X-ray diffraction methods by using the scattering factors calculated from d -orbital functions. The high- and low-spin states of transition-metal atoms in the crystal field O_h in KMf_3 crystals ($M = \text{Mn, Fe, Co}$) were examined and the atoms were shown to occupy the high-spin state by comparing the difference densities and R factors of the refinements, which were calculated by assuming both spin states (Kijima, Tanaka & Marumo, 1981, 1983; Miyata, Tanaka & Marumo, 1983). According to crystal-field theory, the d orbitals in an O_h symmetry field are unambiguously defined. However, as the symmetry of the crystal field becomes lower, d orbitals cannot be defined exactly and the number of unknown parameters defining the d orbitals increases. For the mmm symmetry crystal field of Cu^{2+} in KCuF_3 crystals with Jahn-Teller distortion, two d orbitals are expressed in terms of a linear combination of d_{z^2} and $d_{x^2-y^2}$ orbitals (Tanaka, Konishi & Marumo, 1979). The coefficients of the two orbitals were determined by modifying the dummy subroutines in the conventional least-squares program so that the orthonormal relationships between the two d orbitals were retained during the least-squares refinement. In a similar way the d - s hybridized orbitals of the Cu^+ ions in CuAlO_2 crystals were determined and the peaks in the deformation density maps were explained very well by this

model (Ishiguro, Ishizawa, Mizutani, Kato, Tanaka & Marumo, 1983). However, the d orbitals in lower-symmetry crystal fields such as triclinic and monoclinic crystal fields cannot be obtained without using the method described in (A).

The title compound, bis(1,5-diazacyclooctane)-copper(II) nitrate, $[\text{Cu}(\text{daco})_2](\text{NO}_3)_2$, where daco represents 1,5-diazacyclooctane, is a thermochromic complex and orange crystals of its low-temperature form transform reversibly to violet ones at about 368 K. The crystal structure of the low-temperature form was determined by Hoshino, Fukuda, Sone, Tanaka & Marumo (1989), and will be referred to as (B) in the present study. The molecular structure is shown in Fig. 1, together with the atomic labeling. Crystal data are: $P2_1/n$, $a = 7.9040(7)$, $b = 15.694(1)$, $c = 7.0886(7)$ Å, $\beta = 95.36(1)^\circ$, $V = 875.5(1)$ Å³, $Z = 2$. The nitrate anions which occupy axial positions relative to the Cu-N_4 plane are not coordinated to the Cu atom, whereas the two equatorial nitrates are linked to the amino groups through $\text{N-H}\cdots\text{O}$ hydrogen bonds. It is mentioned in (B) that weakening of the hydrogen bonds by the enhanced thermal motion associated with increased temperature is one of the causes of the initiation of the conformational interconversion of ligands.

Powder UV-visible reflectance spectra measured at temperatures between 305.5 and 372.3 K (Yamaki, Fukuda & Sone, 1982; Yamaki & Fukuda, 1981), and single-crystal visible spectra measured at 298 and 370 K in (B) indicate that remarkable structural changes occur upon phase transition. Infrared spectra measured in (B) at 297 and 369 K showed peaks

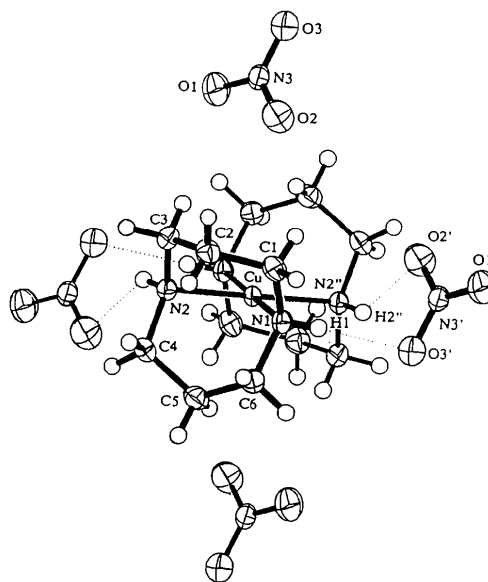


Fig. 1. Molecular structure of $[\text{Cu}(\text{daco})_2](\text{NO}_3)_2$ (Hoshino *et al.*, 1989).

assignable to N—H stretching and deformation modes became stronger at 369 K. EPR spectra of the low- and high-temperature forms also measured in (B) showed that the phase transition causes a decrease in the anisotropy of g values, indicating that the crystal field becomes more isotropic after the phase transition. However, the origin of the thermochromism was not specified since the crystal structure of the violet high-temperature form could not be determined because the single crystals were reduced to powder upon phase transition. The second aim of the present study is to determine the effect of hydrogen bonding on the deformation density maps and on the d -orbital functions of Cu^{2+} .

Theory

It is worthwhile stating several minor modifications which have been made to the method in (A) due to the introduction of κ parameters.

(a) Orthonormal relationships and κ parameters

The outer-shell orbital functions, ψ_i , are expressed in terms of a linear combination of the basis functions, φ_k , as,

$$\psi_i(\mathbf{r}) = \sum_k c_{ik} \varphi_k(\mathbf{r}), \quad (1)$$

or in matrix notation as,

$$\Psi = C\Phi. \quad (2)$$

In the present study c_{ik} are real numbers and the real d -orbital functions, $d_{x^2-y^2}$, d_{z^2} , d_{yz} , d_{zx} , d_{xy} , are taken as the basis functions φ_1 , φ_2 , ..., φ_5 , respectively. The parameters c_{ik} in (1) fulfill the orthonormal relationships between orbitals as,

$$\sum_k \sum_{k'} c_{ik} c_{jk'} \int \varphi_k \varphi_{k'} d\mathbf{r} = \delta_{ij} \quad (3)$$

where δ_{ij} is the Kronecker delta. The basis functions are expressed as a linear combination of spherical harmonics using the polar coordinates (r , β , γ),

$$\varphi_k(\mathbf{r}) = \sum_m a_m \chi_{nlm}(\mathbf{r}) = R_{nl}(r) \sum_m a_m Y_{lm}(\beta, \gamma) \quad (4)$$

where n , l and m are the principal, azimuthal and magnetic quantum numbers, respectively. a_m are constants and $Y_{lm}(\beta, \gamma)$ are spherical harmonics. Since the set of φ_k are orthonormalized basis functions, the orthonormal condition in (3) becomes,

$$\sum_k c_{ik} c_{jk} = \delta_{ij}. \quad (5)$$

Coppens, Guru Row, Leung, Stevens, Becker & Yang (1979) introduced a parameter κ , which represents expansion ($\kappa < 1$) and contraction ($\kappa > 1$) of

the valence-electron densities calculated for atoms in free space. In the present study κ_i is assigned to each orbital function $\psi_i(\mathbf{r})$. The deformation densities could not be explained without κ_i , which will be discussed later. Since $\psi_i(\mathbf{r})$ are normalized, the normalization condition of $\psi_i(\kappa_i \mathbf{r})$ is,

$$\begin{aligned} \int \psi_i^*(\kappa_i \mathbf{r}) \psi_i(\kappa_i \mathbf{r}) d\mathbf{r} &= \int \psi_i^*(\kappa_i \mathbf{r}) \psi_i(\kappa_i \mathbf{r}) r^2 \sin \beta dr d\beta d\gamma, \\ &= \kappa_i^{-3} \int \psi_i^*(\mathbf{r}') \psi_i(\mathbf{r}') r'^2 \sin \beta dr' d\beta d\gamma, \\ &= \kappa_i^{-3}, \end{aligned} \quad (6)$$

where $\mathbf{r}' = \kappa_i \mathbf{r}$. Therefore, the normalized atomic orbital, $\psi_i(\kappa_i \mathbf{r})$, is expressed as,

$$\psi_i(\kappa_i \mathbf{r}) = \kappa_i^{3/2} \sum_k c_{ik} \varphi_k(\kappa_i \mathbf{r}), \quad (7)$$

and the orthonormal condition is expressed as,

$$\begin{aligned} \int \psi_i^*(\kappa_i \mathbf{r}) \psi_j(\kappa_j \mathbf{r}) d\mathbf{r} &= (\kappa_i \kappa_j)^{3/2} \sum_k \sum_{k'} c_{ik} c_{jk'} S_{ij;kk'}, \\ &= \delta_{ij}, \end{aligned} \quad (8)$$

where $S_{ij;kk'}$ is an overlap integral between the basis functions $\varphi_k(\kappa_i \mathbf{r})$ and $\varphi_{k'}(\kappa_j \mathbf{r})$, and is defined as,

$$S_{ij;kk'} = \int \varphi_k(\kappa_i \mathbf{r}) \varphi_{k'}(\kappa_j \mathbf{r}) r^2 \sin \beta dr d\beta d\gamma. \quad (9)$$

Since the integral values of the radial part of (9), $\int R_{nl}(\kappa_i r) R_{nl}(\kappa_j r) r^2 dr$, are common to all (i, j) terms of $S_{ij;kk'}$ and since κ_i is correlated only with $R_{nl}(r)$, the orthogonal relationships between basis functions φ_k and $\varphi_{k'}$ hold as for those between basis functions without κ parameters. Therefore when k is not equal to k' ,

$$S_{ij;kk'} = 0, \quad (10)$$

and the remaining non-zero terms $S_{ij;kk}$ are rewritten as,

$$S_{ij} = S_{ij;kk}. \quad (11)$$

Then the orthonormal condition in (8) is written,

$$(\kappa_i \kappa_j)^{3/2} S_{ij} \sum_k c_{ik} c_{jk} = \delta_{ij}. \quad (12)$$

Since S_{ij} , κ_i and κ_j are not zero,

$$\sum_k c_{ik} c_{jk} = 0, \quad (13)$$

when i is not equal to j . Since S_{ii} is equal to κ_i^{-3} , the normalization condition (12) reduces to

$$\sum_k c_{ik} c_{ik} = 1. \quad (14)$$

From (13) and (14) the orthonormal condition for d orbitals modified by κ_i is evidently identical to (5), which is the orthonormal condition without κ_i parameters. Therefore the introduction of κ_i does not alter the orthonormal condition between atomic orbitals and all the discussions in (A) hold in the present d -orbital analysis.

(b) *Basic relationships between d-orbital functions and scattering factors*

From (39) in (A), the scattering factor of the i th orbital in (1) is expressed as

$$f_i(\mathbf{S}, \kappa_i) = \int \psi_i(\kappa_i \mathbf{r}) \exp[2\pi i \mathbf{S} \cdot \mathbf{r}] \times \psi_i(\kappa_i \mathbf{r}) r^2 \sin \beta \, dr \, d\beta \, d\gamma, \quad (15)$$

where $|\mathbf{S}| = 2 \sin \theta / \lambda$. If we put $\mathbf{r}' = \kappa_i \mathbf{r}$, then (15) is rewritten from (7) as,

$$\begin{aligned} f_i(\mathbf{S}, \kappa_i) &= \kappa_i^{-3} \int \psi_i(\mathbf{r}') \exp[2\pi i (\mathbf{S}/\kappa_i) \cdot \mathbf{r}'] \\ &\quad \times \psi_i(\mathbf{r}') r'^2 \sin \beta \, dr' \, d\beta \, d\gamma, \\ &= \sum_{k, k'} c_{ik} c_{ik'} f_{kk'}(\mathbf{S}/\kappa_i), \\ &= f_i(\mathbf{S}/\kappa_i), \end{aligned} \quad (16)$$

where

$$\begin{aligned} f_{kk'}(\mathbf{S}/\kappa_i) &= \int \varphi_k(\mathbf{r}) \exp[2\pi i (\mathbf{S}/\kappa_i) \cdot \mathbf{r}] \\ &\quad \times \varphi_{k'}(\mathbf{r}) r^2 \sin \beta \, dr \, d\beta \, d\gamma, \\ &= \sum_{m, m'} a_m a_{m'} g_{mm'}, \end{aligned} \quad (17)$$

where $g_{mm'}$ is defined using (4) as,

$$\begin{aligned} g_{mm'} &= \int \chi_{nlm}(\mathbf{r}) \exp[2\pi i (\mathbf{S}/\kappa_i) \cdot \mathbf{r}] \\ &\quad \times \chi_{nlm'}(\mathbf{r}) r^2 \sin \beta \, dr \, d\beta \, d\gamma. \end{aligned} \quad (18)$$

$g_{mm'}$ is calculated using the equation (Weiss & DeMarco, 1958; Iwata, 1977),

$$\begin{aligned} g_{mm'} &= \sum_{k=0} \sum_{M=-k}^k i^k \langle j_k \rangle_{nl} [2(2k+1)]^{1/2} C^k(lm, l'm') \\ &\quad \times \Theta_{kM}(\beta) \exp(iM\gamma), \end{aligned} \quad (19)$$

where $c^k(lm, l'm')$ is defined as,

$$\begin{aligned} c^k(lm, l'm') &= [4\pi/(2k+1)] \int Y_{lm}^*(\beta, \gamma) Y_{k,M}(\beta, \gamma) \\ &\quad \times Y_{l'm'}(\beta, \gamma) \sin \beta \, d\beta \, d\gamma. \end{aligned} \quad (20)$$

Only the terms in (19) which fulfill the following conditions have non-zero values,

$$k+l+l' = \text{even}, \quad |l-l'| \leq k \leq l+l', \quad M = m - m',$$

$\langle j_k \rangle_{nl}$ are tabulated in *International Tables for X-ray Crystallography* (1974, Vol. IV). In the program LINKT90 the scattering factors of orbitals with $l=0$ to $l=4$ can be calculated. The scattering factor for the total number of d electrons is,

$$f_{nd}(\mathbf{S}) = \sum_i p_i f_i(\mathbf{S}/\kappa_i), \quad (21)$$

where p_i is the number of electrons in the i th orbital. Symmetry restrictions imposed by the crystal field on the parameters c_{ik} were summarized in (A).

From (17) and (19) $f_{kk'}$ is expressed in terms of $\langle j_L \rangle_{nl}$ as follows,

$$f_{kk'}(\mathbf{S}/\kappa_i) = \sum_L A_L(\beta, \gamma) \langle j_L(\mathbf{S}/\kappa_i) \rangle_{nl}, \quad (22)$$

where $L=0, 2, 4$ for d electrons. $A_L(\beta, \gamma)$ is listed in Table 2 of (A). $\langle j_L \rangle_{nl}$ is a function of S/κ_i and the derivatives,

$$\partial \langle j_L(\mathbf{S}/\kappa_i) \rangle_{nl} / \partial \kappa_i = -(S/\kappa_i^2) \partial \langle j_L(\mathbf{S}/\kappa_i) \rangle_{nl} / \partial (S/\kappa_i), \quad (23)$$

are necessary for least-squares refinement of κ_i . Using the Hartree-Fock wavefunctions of Mann (1968), $\partial \langle j_L(\mathbf{S}) \rangle_{nl} / \partial S$ were calculated by numerical differentiation for each $\sin \theta / \lambda$ value ranging from 0.0 to 2.0 \AA^{-1} in intervals of 0.05 \AA^{-1} by the program *SFMANN* coded by the author, and were used in the refinement.

(c) *The role of κ parameters in the d-orbital analysis*

As described in (A) identical κ_i values for all d orbitals make the determination of c_{ik} impossible since any unitary transformation U of the set of d orbitals Ψ in (2) does not alter the electron density as shown below,

$$\begin{aligned} \rho(\mathbf{r}) &= (U\Psi)^*(U\Psi) = (UC\Phi)^*(UC\Phi) \\ &= \Phi^* C^* U^* UC \Phi = \Phi^* C^* C \Phi = \Psi^* \Psi. \end{aligned} \quad (24)$$

However, (24) does not hold in the present case, since different κ_i values make the basis functions $\varphi_k(\kappa_i \mathbf{r})$ of $\psi_i(\kappa_i \mathbf{r})$ in (7) different from those of the other $\psi_j(\kappa_j \mathbf{r})$ ($j \neq i$) and no common set of basis functions Φ exists. This means the unitary transformation in (24) will destroy the orthonormal relationships between $\psi_i(\kappa_i \mathbf{r})$. Accordingly, different κ_i values assigned to each d orbital overcome the ambiguity described here.

As described in (42) of (A), if all the κ_i values of the five d orbitals are equal to κ , then (21) becomes,

$$f_{3d}(\mathbf{S}) = p \sum_k f_{kk}(\mathbf{S}/\kappa) + \sum_i \sum_k \sum_{k'} (p_i - p) c_{ik} c_{ik'} f_{kk'}(\mathbf{S}/\kappa), \quad (25)$$

where p is an arbitrary number, and if we put

$$p_1 = 1, \quad p_2 = p_3 = p_4 = p_5 = p = 2,$$

then (25) is changed to,

$$f_{3d}(\mathbf{S}) = 2 \sum_k f_{kk}(\mathbf{S}/\kappa) - \sum_k \sum_{k'} c_{1k} c_{1k'} f_{kk'}(\mathbf{S}/\kappa). \quad (26)$$

Therefore, only the coefficients, c_{1k} , for the hole orbital of Cu^{2+} can be determined by X-ray diffraction methods. However, different κ_i values also destroy the relation in (26) and all the c_{ik} become adjustable parameters.

(d) *Löwdin reorthogonalization method*

After each cycle of refinement, a normalized but not orthogonalized set of orbitals ξ_i is obtained. The reorthogonalized orbital ψ_i is calculated using

Löwdin's method (Löwdin, 1950) as follows,

$$\psi_i = \xi_i - \frac{1}{2} \sum_p \xi_p T_{pi} + \frac{1}{8} \sum_p \sum_q \xi_p T_{pq} T_{qi} + \dots, \quad (27)$$

where

$$T_{st} = \int \xi_s(\kappa_s \mathbf{r}) \xi_t(\kappa_t \mathbf{r}) d\mathbf{r} - \delta_{st}. \quad (28)$$

Using (9) and (12), T_{st} becomes,

$$T_{st} = (1/\kappa_s)^3 \int \xi_s(\mathbf{r}) \xi_t(\kappa_t \mathbf{r}/\kappa_s) d\mathbf{r} - \delta_{st}. \quad (29)$$

T_{st} is not zero because κ_s and κ_t are not equal to each other. The integral in (29) is calculated by numerical integration.

(e) Explicit form of the ill-condition modifier R

The orthonormal relationships were incorporated into the least-squares method in (A) and the final equation is,

$$(I - R)(A' M_f^{-1} A \mathbf{x} - A' M_f^{-1} \mathbf{f}) = 0, \quad (30)$$

where I , A and M_f are the unit matrix, design matrix and variance-covariance matrix, respectively, and \mathbf{f} is a vector having the differences between observed and calculated structure factors for each reflection as its elements. (30) is the same as the conventional secular equation except for R , the ill-condition modifier.

If the number of parameters, basis functions and AO's to be determined are P , N and M , respectively, then the matrix R , of dimension (P, P) , is expressed in terms of the (P, MN) matrix R_i ($i = 1, 2, \dots, M$) as (29) of (A),

$$R' = (O_{p, p-MN}, R'_1, R'_2, \dots, R'_M), \quad (31)$$

where the transposed matrix is denoted by ' and the parameters c_{ik} are assumed to be placed at the bottom of the array of variables. $O_{p, p-MN}$ is a $(P, P-MN)$ matrix with all its elements 0. R_i is

expressed as,

$$R_i = \frac{1}{2} C' M_i. \quad (32)$$

M_i is the (M, P) matrix with all its elements zero except for the following ones,

$$(M_i)_{j,k} = c_{ik} \text{ for } P - MN + (j-1)N + 1 \leq k \leq P - MN + jN, \text{ (for } i \neq j) \quad (33)$$

$$(M_i)_{j,k} = c_{jk} \text{ for } P - MN + (i-1)N + 1 \leq k \leq P - MN + iN, \text{ (for } i \neq j) \quad (34)$$

$$(M_i)_{i,k} = 2c_{ik} \text{ for } P - MN + (i-1)N + 1 \leq k \leq P - MN + iN, \text{ (for } i \neq j). \quad (35)$$

Refinement

(a) Refinement with spherical scattering factors

The reflection data measured in (B) were used in the present study. Experimental conditions were summarized in (B). Atomic parameters determined in (B) were used as the starting set for the analyses in the subsequent stage. Neutral atomic scattering factors of C, N and O atoms, and ionic atomic scattering factors for Cu^{2+} and O^- are taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The Cu and O atoms in the NO_3^- groups were assumed to have charges $+2$ and $-\frac{1}{3}e$, respectively. After refinement with 2948 independent reflections allowing for a Gaussian isotropic type I extinction effect, $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ and $R_2 = [\sum (|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2}$ were 0.0335 and 0.0366, respectively. The weights of all reflections were fixed at 1.0. Refinement with a type II isotropic extinction effect converged to R_1 and R_2 , 0.037 and 0.046, respectively. Therefore, refinement assuming a

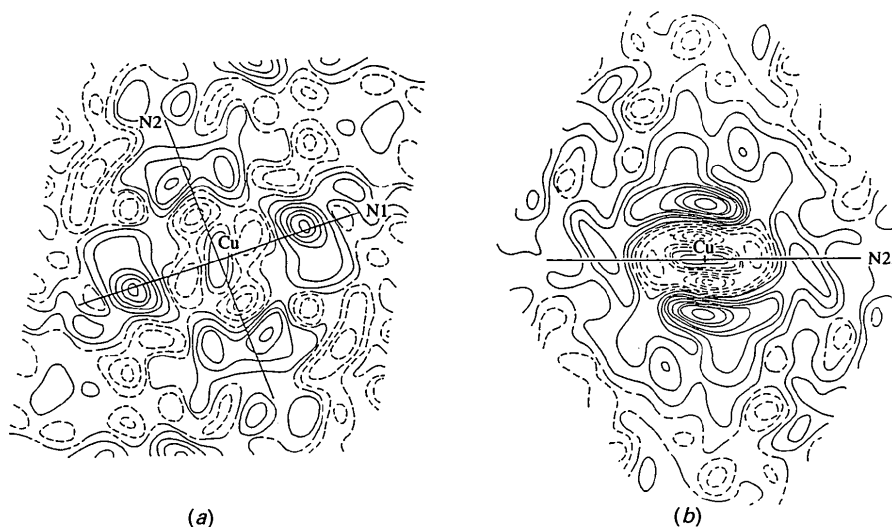


Fig. 2. Deformation densities after spherical-atom refinement with ionic Cu^{2+} and NO_3^- in (a) the Cu-N_4 coordination plane and in (b) the plane perpendicular to it. Contours at $0.05 \text{ e } \text{\AA}^{-3}$, zero and negative contours in dashed-dotted and broken lines, respectively.

Table 1. *3d-orbital parameters* c_{ik} 's of Cu^{2+}

The quantization axes are defined as:
 $x_q = 0.03307\mathbf{a} - 0.05523\mathbf{b} + 0.06346\mathbf{c}$,
 $y_q = -0.10819\mathbf{a} - 0.02637\mathbf{b} - 0.05673\mathbf{c}$,
 $z_q = 0.05789\mathbf{a} - 0.01777\mathbf{b} - 0.11323\mathbf{c}$.

<i>i</i>	p_i	κ_i	$d_{x^2-y^2}$	d_{z^2}	d_{yz}	d_{zx}	d_{xy}
(a) Calculated values from the model of ligands with point charges							
1	1.0	1.0	0.99856	-0.04978	-0.00510	-0.01759	-0.00783
2	2.0	1.0	0.01285	0.39740	0.01844	0.00887	-0.91733
3	2.0	1.0	-0.01855	-0.03240	-0.65156	-0.75689	-0.03472
4	2.0	1.0	-0.04604	-0.90216	-0.09907	0.14301	-0.39208
5	2.0	1.0	-0.01568	-0.15698	0.75187	-0.63741	-0.05927
(b) Observed values from X-ray <i>d</i> -orbital analysis							
1	1.0	0.97 (11)	0.75 (34)	0.21 (59)	0.23 (216)	0.57 (79)	0.10 (79)
2	2.0	1.37 (7)	0.08 (28)	0.12 (17)	-0.19 (19)	0.10 (26)	-0.97 (6)
3	2.0	0.81 (5)	0.63 (22)	-0.15 (52)	-0.44 (44)	-0.61 (34)	-0.06 (22)
4	2.0	0.71 (4)	0.04 (32)	-0.93 (13)	-0.10 (29)	0.34 (41)	-0.06 (10)
5	2.0	0.90 (5)	0.15 (76)	-0.22 (45)	0.84 (43)	-0.42 (85)	-0.22 (15)

Gaussian anisotropic type I extinction effect (Becker & Coppens, 1974*a,b*, 1975) was carried out, and the R_1 and R_2 values were reduced to 0.0311 and 0.0313, respectively. $S = [\sum(|F_o| - |F_c|)^2 / (m - n)]^{1/2}$ was 0.756, where m and n are the number of reflections and the number of variables, respectively. The deformation density in the Cu-N₄ coordination plane and in the plane perpendicular to it which passes through Cu and two N(2) atoms related by the inversion centre on Cu^{2+} are illustrated in Figs. 2(a) and 2(b), respectively.

(b) *d*-orbital analysis

The atomic orbitals were divided into core orbitals and outer-shell orbitals. Scattering factors of electrons in the Ar core and the *d*-orbital scattering factors $\langle j_0 \rangle_{3d}$, $\langle j_2 \rangle_{3d}$ and $\langle j_4 \rangle_{3d}$ of the Cu^{2+} ion in (19) were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

The point-group symmetry of the Cu-atom site is 1 and accordingly there are no restrictions on the coefficients c_{ik} . All 25 c_{ik} and five κ_i and p_i in (21) were adjusted in the least-squares procedure, which incorporated the orthonormal relationships between *d* orbitals. Since overlap density is ignored in the present study, the matrix P in (A) having overlap integrals between molecular orbitals as its elements is taken as the unit matrix. The number of electrons in each orbital was fixed to a proper integer between 0 and 2 to fulfill the single Slater determinant representability.

Since the least-squares method for non-linear problems requires approximate values of c_{ik} as the starting set, they were calculated by taking the crystal fields as the perturbation (Kamimura, Sugano & Tanabe, 1969) using the program *WAVE85* coded by the author. The crystal-field potential was calculated by assigning a point charge to each atom. The starting set is listed in Table 1(a). In the present study *d*-orbital analysis was carried out taking the x axis of quantization along the line from Cu^{2+} to the top of the larger negative peak around Cu^{2+} in Fig. 2(a), and taking the z axis along the direction perpendicular to the coordination plane. The axes are defined explicitly in Table 1. We call the *d* orbitals which have dominantly large coefficients c_{ik} of the $d_{x^2-y^2}$ and d_{xy} basis functions in (7) the $d_{x^2-y^2}$ -like and d_{xy} -like orbitals, respectively. In order to make sure that the hole orbital of Cu^{2+} (d^9) is a $d_{x^2-y^2}$ -like orbital, p_i were refined keeping the sum of p_i equal to 9. When p_i exceeded 2 in the refinement, it was then fixed at 2. The $d_{x^2-y^2}$ -like and d_{xy} -like orbitals remained unfixed having p_i values between 1 and 2. Since the p_i of a $d_{x^2-y^2}$ -like orbital is smaller than that of a d_{xy} -like orbital, it was fixed at 1 and the other at 2. Then the set of κ_i values were refined with

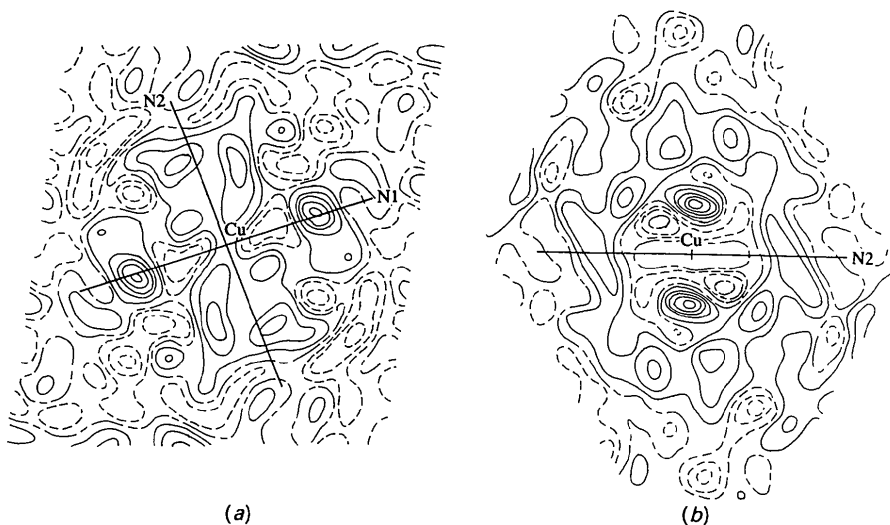


Fig. 3. Difference densities after 3*d*-orbital analysis in (a) the Cu-N₄ coordination plane and in (b) the plane perpendicular to it. Contour intervals are the same as those in Fig. 2.

the scale factors fixing all other parameters. All parameters except the c_{ik} were refined subsequently, and after that only the set of c_{ik} and the scale factor were refined simultaneously suppressing shifts of c_{ik} to between 0.01 and 0.05 of the calculated values. This procedure was repeated. c_{ik} and all derivatives $\partial F/\partial c_{ik}$ in the matrix A in (30) were calculated as double-precision variables. After each cycle of refinement the d -orbital functions were reorthogonalized using Löwdin's method described in the foregoing section. This procedure is necessary, since Lagrange's method employed in the present least-squares method only gives the necessary condition. The Schmidt orthogonalization method did not work well since the first orbital calculated dominates the remaining ones. Löwdin's method treats the five d orbitals with equal weight. R_1 , R_2 and S are 0.0299, 0.0299 and 0.722, respectively. The values of c_{ik} are listed in Table 1(b). c_{ik} shifts in the refinement do not reduce to zero. Therefore, when the refinement reached the stage where S did not reduce any more, the refinement was judged to have converged. The difference density maps after the refinement are shown in Figs. 3(a) and 3(b).

(c) Anharmonic thermal-vibration analysis

Since significant peaks and troughs were revealed near Cu^{2+} in Fig. 3(b), and since there is no effective intermolecular contact with Cu^{2+} along the z axis of quantization, the vibration along this direction is expected to be relatively free and large anharmonic vibration is expected. Therefore, refinement assuming anharmonic vibration of Cu^{2+} was carried out using the method of Tanaka & Marumo (1983). Since the point-group symmetry of Cu^{2+} is C_i , the 15 fourth-order anharmonic parameters were refined. The harmonic parameters were fixed to avoid severe interaction with the harmonic ones. Since the peaks resulting from the anharmonic vibration of Cu^{2+} were comparable with those of the aspherical peaks of the d orbitals in Fig. 2(a), c_{ik} were refined again and are listed in Table 1(b). c_{ik} with significant values are underlined in the table. The maximum value of the ratio of the shifts to e.s.d.'s of c_{ik} at this stage of the refinement is 0.39 for c_{42} . Next, the anharmonic parameters were refined again. The final coordinates of the non-H atoms are listed in Table 2(a).* The R_1 , R_2 and S values were 0.0296, 0.0297 and 0.721,

* Lists of structure factors, atomic parameters of H atoms (Table 2b), anisotropic temperature factors of non-H atoms (Table 2c), extinction parameters (Table 2d) and potential parameters of Cu^{2+} (Table 3), and Fig. 4 illustrating the potential around Cu^{2+} have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71294 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2(a). Fractional atomic coordinates and equivalent temperature factors (\AA^2)

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq}
Cu	0.0	0.0	0.0	1.821 (7)
N(1)	0.0664 (2)	-0.11026 (8)	0.1266 (2)	2.30 (3)
N(2)	-0.2148 (2)	-0.06144 (8)	-0.1059 (2)	2.25 (3)
N(3)	-0.1418 (2)	-0.4094 (1)	0.0150 (2)	2.99 (3)
O(1)	-0.0834 (3)	-0.3838 (2)	0.1723 (3)	5.16 (5)
O(2)	-0.2284 (2)	-0.4749 (1)	-0.0014 (4)	4.87 (5)
O(3)	-0.1178 (3)	-0.3685 (1)	-0.1318 (4)	5.56 (5)
C(1)	-0.0542 (2)	-0.1298 (1)	0.2700 (2)	2.99 (4)
C(2)	-0.2330 (2)	-0.1499 (1)	0.1852 (3)	3.22 (4)
C(3)	-0.3160 (2)	-0.0820 (1)	0.0554 (3)	2.97 (4)
C(4)	-0.1794 (2)	-0.1371 (1)	-0.2244 (2)	2.70 (4)
C(5)	0.0082 (2)	-0.1587 (1)	-0.2091 (2)	3.09 (4)
C(6)	0.0873 (2)	-0.1806 (1)	-0.0117 (2)	2.81 (4)

respectively. The average potential $V(\mathbf{u})$ of Cu^{2+} derived from the temperature factors including the anharmonic terms is

$$V(\mathbf{u}) = \frac{1}{2} \sum_i b_i u_i^2 + \sum_i \sum_j \sum_k q_{ijk} u_i^2 u_j u_k, \quad (36)$$

where $\mathbf{u} = (u_1, u_2, u_3)$ is the displacement vector from the equilibrium position of Cu^{2+} . i, j, k run from 1 to 3 and any permutation among them is permitted. The potential parameters b_i and q_{ijk} are listed in Table 3.*

Results and discussion

(a) Hydrogen bonds and deformation density after spherical-atom refinement

The Cu atom is located on the center of symmetry and it is coordinated square planarly to the four N atoms. The bond lengths of Cu—N(1) and Cu—N(2), 1.995 (2) and 2.034 (2) \AA , respectively, are significantly different from each other and the bond angle N(1)—Cu—N(2) is 85.92 (7)°. There are two NO_3^- ions above and below the Cu—N₄ coordination plane. The closest contact of these ions to Cu^{2+} is that of Cu—O(2), 4.338 \AA . Therefore, these two groups have little effect on the crystal field of the Cu atom. However, the two NO_3^- ions at either side of the coordination plane affect the crystal field through the hydrogen bonds N(1)—H(1)⋯O(3)' and N(2)''—H(2)''⋯O(2)' in Fig. 1. The distances of N(1)⋯O(3)' and N(2)''⋯O(2)' are 2.911 (2) and 3.093 (2) \AA , respectively. The angles N(1)—H(1)⋯O(3)' and N(2)''—H(2)''⋯O(2)' are 161 (2) and 136 (2)°, respectively. As pointed out in (B), the hydrogen bond N(1)—H(1)⋯O(3)' is much stronger than N(2)''—H(2)''⋯O(2)' resulting in a shorter Cu—N(1) bond compared with Cu—N(2). The daco ring has a non-crystallographic mirror plane determined by C(2), Cu and C(5). C(1), N(1) and

* See deposition footnote.

C(6) approximately overlap with atoms C(3), N(2) and C(4), respectively, by this operation. Thus the difference in the Cu—N bond lengths can be attributed to hydrogen-bond formation. The hydrogen bonds are also responsible for the longer N(3)'—O(3)' bond, 1.254 (4) Å, relative to the N(3)'—O(2)' bond, 1.232 (4) Å, in NO₃⁻. The N(3)'—O(2)' bond length is practically equal to that of the N(3)'—O(1)' bond, 1.234 (4) Å, in which O(1)' has no such intermolecular interactions. These facts indicate that more electron density is donated from the NO₃⁻ group to the N(1)—H(1) moiety than to N(2)—H(2) through the hydrogen bond.

It is very interesting to look at how these effects appear in the deformation density map after spherical-atom refinement. The hole orbital of the Cu²⁺ ion appears as four negative peaks in Fig. 2(a). Distortion of the Cu—N bond lengths and N—Cu—N bond angles from tetragonal symmetry due to the hydrogen bonds is reflected directly in these peaks, though the lines between the origin and the tops of these peaks intersect approximately at right angles. The negative peaks near the shorter Cu—N(1) bond are shallower than those near the longer Cu—N(2) bond. The positive peaks on the Cu—N bonds in the vicinity of the N atoms also correlate with the strength of the Cu—N bonds. The peak on the Cu—N(1) bond is larger than that on the Cu—N(2) bond indicating more electrons are donated from the NO₃⁻ group to N(1) through the stronger hydrogen bonds, which results in a stronger Cu—N(1) coordination bond. The deformation map in Fig. 2(b) shows a much larger discrepancy from the spherical-atom model. This will be shown to be due to expansion of the *d* orbitals along the direction of the *z* axis of quantization.

(b) *d*-orbital analysis and the difference densities

Since there is a hole orbital in Cu²⁺ with the *d*⁹ electron configuration, the preliminary refinement was carried out assuming the hole orbital to be the *d*_{*x*²-*y*²} orbital which has the shape of four equivalent lobes perpendicular to each other. The heights of the four negative peaks were reduced; however, there still remained four negative peaks with more than half the heights of those in Fig. 2(a). Thus it became evident that the negative peaks in Fig. 2(a) did not originate mainly from anisotropy of the thermal vibration of the Cu atom but from *d* orbitals of a more complex form. Distortion of the four peaks in the coordination plane from that expected for *d*_{*x*²-*y*²} electrons cannot be explained by mixing *d*_{*x*²-*y*²} and *d*_{*xy*} orbitals, which simply has the effect of rotating the four peaks and does not deform the four equivalent electron lobes. However, the distortion can be explained by the combination of orbitals with differ-

ent κ_i values, which span the *xy* plane. Therefore, analysis of the *d* wavefunction in the *C_i* crystal field was carried out using the method described in (A).

The difference density after refinement of κ_i and *c_{ik}* is illustrated in Fig. 3. Most of the negative peaks around the Cu atom in Fig. 2(a) disappeared and the large negative and positive peaks along the *z* axis in Fig. 2(b) were almost deleted. These peaks would not disappear without κ_i parameters. However, new peaks emerged near Cu²⁺ in Figs. 3(a) and 3(b), which led us to analyse the anharmonic vibration of Cu²⁺. The values of *c_{ik}* in Table 1(b) show that the *d*_{*x*²-*y*²} and *d*_{*xy*} orbitals are the main contributors to orbitals 1 and 2, respectively. Thus, the two orbitals are located mainly in the coordination plane, while the other three orbitals are distributed mainly along the directions perpendicular to the coordination plane. The κ_i values of these orbitals are less than 1, indicating these orbitals are expanded compared with those of the free atoms calculated by Mann (1968) along the *z* direction, where effectively no coordinated ligands exist. Orbital 1 is contracted in the square-planar coordination plane, and κ_2 of orbital 2 is approximately equal to 1. Refinement of κ_i assigned to each *d* orbital was remarkably successful as shown in Fig. 3(b), and the importance of the expansion and contraction effects of each *d* orbital in the ligand field is clearly demonstrated. The analysis as well as the role in the least-squares refinements discussed in the foregoing section make κ_i , assigned to each atomic orbital, one of the most important parameters in the X-ray AO analysis.

d-orbital analysis converged as shown in Table 1(b), though the e.s.d. of each *c_{ik}* is large. Judging from the difference between Figs. 2 and 3, most of the reduction of *R*₁, *R*₂ and *S* from the spherical-atom refinement seems to be due to refinement of the κ_i parameters. However, all the largest *c_{ik}* of the *d* orbitals have significant values. The large e.s.d.'s of small *c_{ik}* are evidently due to the small effect they have on the structure factors, which is negligible or comparable with the error of measurement of *F_o*, since the effect is proportional to *c_{ik}*². However, the smaller *c_{ik}* can possibly have a significant effect on *F_c* when combined with the larger values through the *c_{ik}c_{ik'}* terms in (16). Therefore, all the parameters *c_{ik}* are expected to be able to be determined as in the case of much simpler complexes such as KCuF₃ (Tanaka, Konishi & Marumo, 1979) if more accurate structure factors are measured. Measurements at lower temperatures are necessary for complexes with many light atoms such as the one studied in the present paper. However, shifts in *c_{ik}* at the final stage of refinement are all smaller than their e.s.d.'s. Most of the ratios of shift to e.s.d. are less than 0.3. Shifts of *c_{ik}* with significant values are less than 0.1. The four negative lobes in Fig. 2(a), and the positive and

negative peaks in Fig. 2(b) reduced significantly after refinement, indicating that the refinement had converged successfully. It is to be noted that there always exists another solution set with the signs of all c_{ik} reversed.

(c) *Anharmonic thermal vibration and difference density*

The peaks which appeared in Fig. 3(b) after refinement of κ_i were shown to be due to anharmonic thermal vibration of the Cu atom. Analysis of the anharmonic vibration as well as of the c_{ik} before refinement of the κ_i parameters did not affect the dominantly large peaks in Fig. 2(b). Peaks overlapped by the larger electron density due to the aspherical electron configuration were also revealed in KCuF_3 (Tanaka, Konishi & Marumo, 1979) and CuAlO_2 (Ishiguro, Ishizawa, Mizutani, Kato, Tanaka & Marumo, 1983) crystals. The number of significant potential parameters is eight out of a total of 15 parameters. The potential in the same plane as that in Fig. 2(b) was calculated using these significant parameters and is illustrated in Fig. 4.* The positive potential corresponds to the negative peaks in Fig. 3(b) and *vice versa*. Reductions in R_1 , R_2 and S are very small; however, after anharmonic vibration analysis the peaks in Fig. 3(b) disappeared as shown in Figs. 5(a) and 5(b), indicating the refinement was successful.

Concluding remarks

The d -orbital functions of Cu^{2+} in the crystal field C_4 were successfully obtained by X-ray AO analysis, by

* See deposition footnote.

utilizing the least-squares method incorporating orthonormal relationships between the d -orbital functions. As mentioned in the foregoing section, κ_i parameters work to avoid the ambiguity caused by any unitary transformation of the set of AO and make X-ray d -orbital analysis possible. The X-ray AO analysis should therefore begin with that of κ_i parameters if the approximate values of AO and the occupation number of each AO are known beforehand, for example, by relatively simple quantum-mechanical calculations such as that described in the present study. If the occupancy numbers are not clearly known, they can be refined first and subsequently fixed to 2 or 0 when they become larger than 2 or when they become negative during the refinement, respectively. Then the occupancy numbers of the remaining orbitals can be assigned to the nearest integer values of the refined values taking into account the total number of d electrons. The orthonormal conditions and the integer occupation numbers correspond to the idempotency condition imposed in the method of determination of reduced density matrices utilizing the structure factors measured by the X-ray diffraction method (Clinton, Frishberg, Massa & Oldfield, 1973).

The author is indebted to Professor Y. Fukuda of Ochanomizu University for his discussion on the thermochromism of the title compound. Research support from Research Foundation for Electrotechnology of Chubu, and Izumi Science and Technology Foundation are gratefully acknowledged. This work has been partly supported by a Grant-in-Aid for Scientific Research from Ministry of Education, Science and Culture.

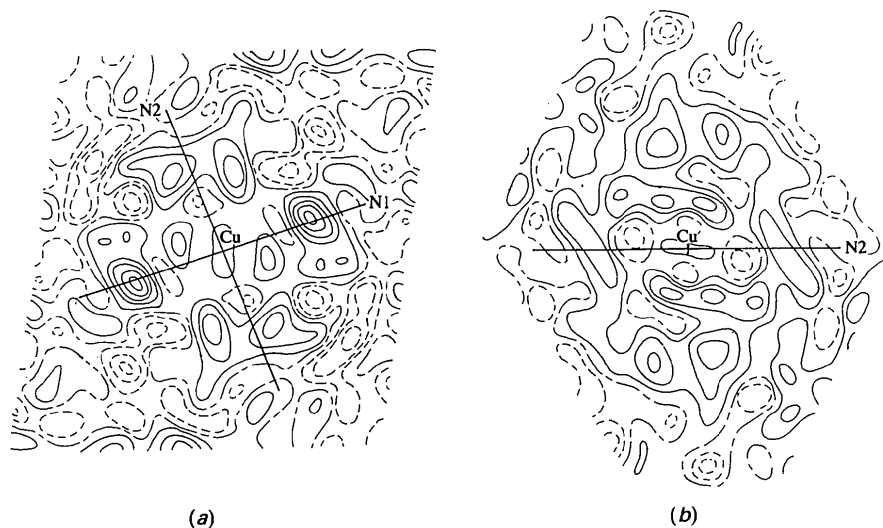


Fig. 5. Difference densities after the anharmonic vibration analysis of Cu^{2+} in (a) the Cu-N_4 coordination plane and in (b) the plane perpendicular to it. Contour intervals are the same as those in Fig. 2.

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Crystalline-State Reaction of Cobaloxime Complexes. 17. Requirements for Racemization of the Bulky Dimethoxycarbonylethyl Group

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(Received 18 March 1993; accepted 5 July 1993)

Abstract

Two crystal structures, [(*R*)-1,2-dimethoxycarbonylethyl]bis(dimethylglyoximato)(*R*)-phenylethylamine]cobalt(III) (*R*-pea) and [(*R*)-1,2-dimethoxycarbonylethyl]bis(dimethylglyoximato)(1-propylamine)cobalt(III) methanol solvate (pa), have been determined. *R*-pea: [Co(C₄H₇N₂O₂)₂(C₆H₉O₄)(C₈H₁₁N)], *M_r* = 555.5, monoclinic, *P*2₁, *a* = 9.125 (1), *b* = 15.820 (2), *c* = 9.348 (1) Å, β = 102.57 (1)°, *V* = 1317.0 (1) Å³, *Z* = 2, *D_x* = 1.40 g cm⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 7.32 cm⁻¹, *F*(000) = 584, *T* = 298 K, *R* = 0.055 and *wR* = 0.049 for 2208 observed reflections. pa: [Co(C₄H₇N₂O₂)₂(C₆H₉O₄)(C₃H₉N)].CH₃OH, *M_r* = 525.4, monoclinic, *P*2₁, *a* = 9.803 (3), *b* = 15.554 (3), *c* = 9.267 (3) Å, β = 117.24 (2)°, *V* = 1255.4 (7) Å³, *Z* = 2, *D_x* = 1.39 g cm⁻¹, λ(Mo *K*α) = 0.71069 Å, μ = 7.66 cm⁻¹, *F*(000) = 556, *T* = 298 K, *R* = 0.070 and *wR* = 0.076 for 1699 observed reflections. Neither crystal was racemized on exposure to X-rays or visible light without crystal degradation. The structures are compared with those of crystals which contain the same chiral alkyl group but a different axial base ligand. Non-reactivity of the two crystals

may be due to the fact that the chiral dimethoxycarbonylethyl groups of the two crystals have too small a cavity for racemization to take place and are not in contact with each other.

Introduction

In serial studies of crystalline-state racemization of bis(dimethylglyoximato)cobalt(III) (cobaloxime) complexes, two kinds of chiral alkyl groups bonded to the Co atom have been found to be racemized on exposure to X-rays or visible light. One group is the (*R*)-1-cyanoethyl (ce) group, [—CH(CH₃)CN] (Ohashi, 1988), while the other is the (*R*)-1-methoxycarbonylethyl (mce) group, [—CH(CH₃)-CO₂CH₃] (Kurihara, Ohashi, Sasada & Ohgo, 1983; Kurihara, Uchida, Ohashi, Sasada & Ohgo, 1984). Recently several cobaloxime complexes have been prepared which contain the bulkier (*R*)-1,2-dimethoxycarbonylethyl (dmce) group (Ohgo, Arai & Takeuchi, 1991). Although the dmce group is much bulkier than the ce and mce groups, the dmce complexes with diphenylmethylphosphine (dpmp) and pyridine (py) as axial base ligands exhibit crystalline-state racemization (Sekine, Sakai, Uchida, Ohashi, Arai, Ohgo, Kamiya & Iwasaki, 1990; Sakai,

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