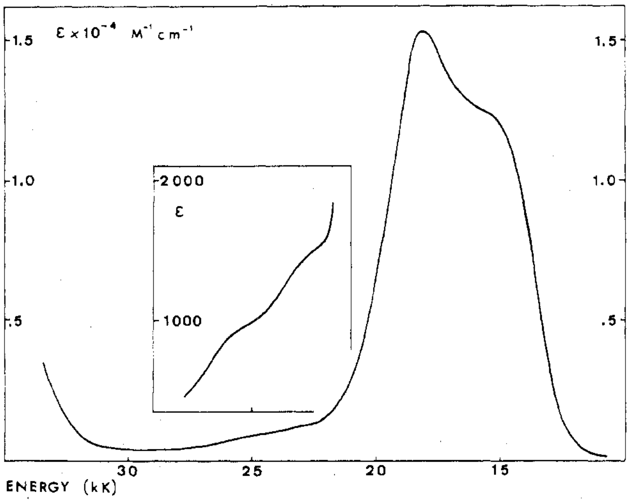

Figure 5. Electronic spectrum of $W_4O_8Cl_8(H_2O)_4^{2-}$ in 12 M HCl. Central portion magnified 5 times in ordinate only.

by the two observed intense intervalence transitions. As far as the latter are concerned, their correct assignment would require the electron correlation knowledge in the mixed-valence complex. Since, on the visible spectroscopy time scale (ca. 10^{-14} s), both d electrons can be considered as localized, one can imagine two possibilities for the ground state, i.e., the two W^V atoms cis or trans with respect to each other. In the present state, further speculation is inappropriate. It is believed that the synthesis of other compounds of the same type but with nonequivalent tungsten atoms will shed some light on this problem. This investigation is now in progress.

Registry No. $[HNMe_3]_2[W_4O_8Cl_8(H_2O)_4]\cdot 2H_2O$, 65027-46-5.

Supplementary Material Available: A listing of structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

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Presence of a Static Jahn–Teller Distortion in Copper(II) Terpyridine Complexes. 1. Crystal Structure of $Cu(terpy)_2(NO_3)_2$

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The crystal and molecular structure of diterpyridinecopper(II) nitrate $[Cu(C_{15}N_3H_{11})_2(NO_3)_2]$ has been determined from three-dimensional single-crystal x-ray diffraction data. The green crystals are tetragonal, space group $I4_1/a$ with eight formula units in the unit cell with $a = 12.476$ (6) and $c = 36.284$ (13) Å. The structure was refined to an R of 0.070 for 1931 independent reflections with $F > 1\sigma(F)$. The CuN_6 octahedra are strongly distorted and exhibit approximately orthorhombic symmetry with Cu–N bond lengths of $\simeq$1.99, 2.08_5, and 2.29 Å, respectively. The geometry is very roughly described as the superposition of a "tetragonal compression" along [001] as the result of the rigid structure of the terpyridine ligands and a "tetragonal elongation" perpendicular to [001] as a consequence of the Jahn–Teller effect. Some of the NCuN bond angles differ distinctly from 90° and the two terpyridine ligands are twisted also but differently in extent. EPR spectroscopic results are included in the Discussion.

Introduction

The σ-antibonding ${}^2E_g$ ground state of Cu^{2+} in octahedral coordination is highly Jahn–Teller unstable and leads to strongly distorted ligand environments. In all cases of stochiometric Cu^{2+} compounds known so far the octahedra become tetragonally elongated—with a small orthorhombic component superimposed—if the following conditions are met:[1,2] (a) the octahedral ligands are identical, (b) the octahedral sites of the host lattice are regular when occupied by non-Jahn–Teller ions. The latter condition can be examined by comparison with the stoichiometrically analogous Ni^{2+} or Zn^{2+} compounds, because these ions possess Jahn–Teller stable A ground states in octahedral coordination and ionic radii and electronic configurations similar to Cu^{2+}.

It is possible, however, to force Cu^{2+} into a tetragonally compressed coordination if the host lattice site itself possesses this kind of distortion. Thus in the mixed crystals $Ba_2Zn_{1-x}Cu_xF_6$ compressed CuF_6 octahedra are observed up to $x \simeq 0.3$.[2] The extent of compression, however, is appre-

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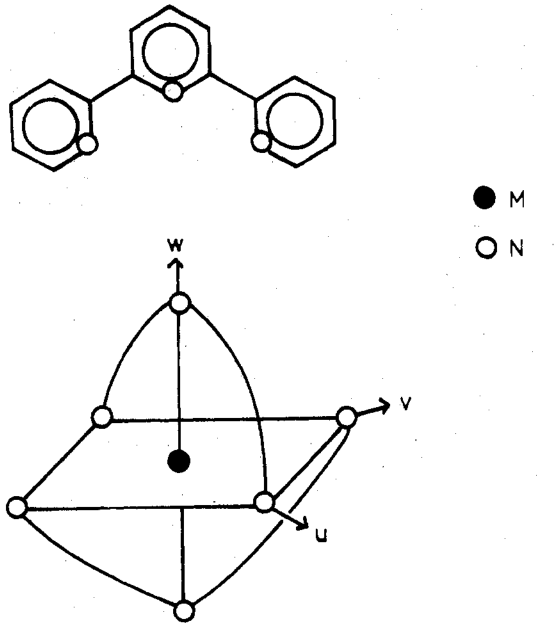

Figure 1. Structure (schematic) of $M(terpy)_2^{2+}$ cations (M: Ni^{2+}, Cu^{2+}, Co^{2+}).

ciably larger than that of the ZnF_6 host lattice sites. It can be concluded that a true Jahn–Teller stabilization in opposite sense to the normal case of a tetragonal elongation has occurred.

It seemed interesting to us to investigate which distortions are induced by Cu^{2+} ions if the compressed coordination octahedra are *isolated* from each other in the unit cell. This is different from the geometric situation in the layer structure of Ba_2ZnF_6 where the ZnF_6 polyhedra are connected with each other via common corners in two dimensions. Terpyridine complexes $M(terpy)_2X_2 \cdot nH_2O$ ($M = Ni^{2+}, Cu^{2+}$; $X^- = Cl^-, Br^-, NO_3^-, ClO_4^-$) represent a class of compounds with isolated MN_6 octahedra (Figure 1), which are likely to be tetragonally compressed in first approximation by the influence of the rigid structure of the tridentate terpyridine ligands. We felt it worthwhile to investigate the symmetry and extent of the Jahn–Teller distortion in the case of $M = Cu^{2+}$, which adds to the host lattice effect just mentioned.

In the following we report the results of a single-crystal x-ray structure analysis of $Cu(terpy)_2(NO_3)_2$. The EPR and ligand field spectroscopic results will be published elsewhere.[3]

Experimental Section

Preparation. $Cu(NO_3)_2 \cdot 3H_2O$ (0.60 g) and 1.16 g of terpyridine were dissolved in 50 mL of boiling water. The green solution was evaporated until green crystals precipitated.[4] They were recrystallized from 15 mL of hot water. When the solution was cooled slowly, dark green plates of $Cu(terpy)_2(NO_3)_2$ were obtained, which were dehydrated in vacuo over P_2O_5. Anal. Calcd for $Cu(C_{15}N_3H_{11})_2(NO_3)_2$: C, 55.1; N, 17.2; H, 3.4. Found: C, 55.2; N, 17.1; H, 3.4.

Structural Analysis. A single crystal of dimensions 0.8 mm [110], 0.5 mm [1$\bar{1}$0], and 0.03 mm [001] was chosen for the structural analysis. By polarization microscopy the optical axis of the tetragonal crystal was found to coincide with the plate normal. The intensities were measured with an automated Philips four-circle diffractometer PW 1100 at 298 K and the data collected up to $\theta_{max} = 25°$ by a $\omega/2\theta$ scan technique (scan width in θ, 1.2°), using Mo Kα (0.71069 Å) radiation (graphite monochromator). The integral intensity and the background on both sides of each reflection were measured. No absorption correction was applied. From the experimental extinction conditions (hkl, $h + k + l = 2n$; $hk0$, $h(k) = 2n$; $00l$, $l = 4n$) the space group $I4_1/a$ could be uniquely deduced. The reflections with odd l were weak and not visible in the powder diagrams, which were taken for comparison with terpyridine complexes with different anions and transition-metal cations. Hence a smaller primitive unit cell with $a' = a/(2^{1/2})$ and $c' = c/2$ resulted from the powder data (pseudo space group $P4_2/n$). The cell dimensions were obtained by a least-squares fit of 20 reflections, which led to a body-centered tetragonal unit cell: $a = 12.476$ (6) and $c = 36.284$ (13) Å with $Z = 8$.

Table I. Positional Parameters for $Cu(terpy)_2(NO_3)_2$

Atom	x	y	z
Cu	0.0	0.75	0.11026 (2)
N_{11}	0.0	0.75	0.0561 (1)
N_{12}	0.1523 (3)	0.6894 (3)	0.0991 (1)
N_{21}	0.0	0.75	0.1658 (1)
N_{22}	−0.0743 (3)	0.5885 (3)	0.1256 (1)
C_{11}	0.0872 (4)	0.7143 (4)	0.0382 (1)
C_{12}	0.0884 (4)	0.7119 (5)	0.0003 (2)
C_{13}	0.0	0.75	−0.0184 (2)
C_{14}	0.1753 (4)	0.6812 (4)	0.0629 (1)
C_{15}	0.2745 (4)	0.6457 (4)	0.0501 (2)
C_{16}	0.3526 (4)	0.6205 (5)	0.0760 (2)
C_{17}	0.3299 (4)	0.6289 (4)	0.1128 (2)
C_{18}	0.2289 (4)	0.6633 (4)	0.1236 (2)
C_{21}	−0.0392 (4)	0.6653 (4)	0.1849 (1)
C_{22}	−0.0426 (5)	0.6645 (5)	0.2231 (1)
C_{23}	0.0	0.75	0.2422 (2)
C_{24}	−0.0791 (4)	0.5749 (4)	0.1620 (1)
C_{25}	−0.1198 (5)	0.4811 (4)	0.1778 (2)
C_{26}	−0.1540 (4)	0.4007 (4)	0.1547 (2)
C_{27}	−0.1504 (5)	0.4136 (4)	0.1172 (2)
C_{28}	−0.1098 (4)	0.5091 (4)	0.1037 (2)
H_{12}	0.148 (5)	0.694 (5)	−0.011 (2)
H_{13}	0.0	0.75	−0.041 (2)
H_{15}	0.285 (5)	0.644 (5)	0.024 (2)
H_{16}	0.421 (5)	0.599 (5)	0.067 (2)
H_{17}	0.384 (5)	0.605 (5)	0.131 (2)
H_{18}	0.215 (5)	0.684 (5)	0.147 (2)
H_{22}	−0.076 (5)	0.603 (5)	0.236 (2)
H_{23}	0.0	0.75	0.266 (2)
H_{25}	−0.120 (5)	0.477 (5)	0.205 (2)
H_{26}	−0.190 (5)	0.335 (5)	0.165 (2)
H_{27}	−0.179 (5)	0.358 (5)	0.098 (2)
H_{28}	−0.104 (5)	0.522 (5)	0.080 (2)
N_1	0.7306 (4)	−0.0434 (4)	0.2143 (1)
O_1	0.8256 (4)	−0.0470 (4)	0.2069 (1)
O_2	0.6948 (5)	0.0301 (4)	0.2328 (1)
O_3	0.6680 (5)	−0.1121 (6)	0.2026 (1)

Reflections hkl and $\bar{h}\bar{k}l$ were measured and, after the usual polarization and Lorentz correction, averaged. From the expected set of 2486 symmetry-independent reflections, 555 had an intensity below the limit of observation ($F_{min} = 1\sigma(F)$; $\sigma(F)$ is derived from $\sigma(I)$, which is the statistical standard deviation of a single measurement). Applying the MULTAN program all atomic parameters except those for two C atoms and the NO_3 groups could be determined. A first refinement, using the x-ray system 72, led to a reliability factor, $R = \sum||F_o| - |F_c||/\sum|F_o|$, of 0.25. The subsequent difference Fourier synthesis yielded all atoms in the asymmetric unit with the exception of the hydrogen atoms. The isotropic refinement at this stage led to $R = 0.12$. The positions of the H atoms were calculated assuming a C–H bond distance of ≈1 Å. The final anisotropic refinement of all atoms with the exception of the H atoms, which were isotropically refined, yielded $R = 0.07_0$. Unit weights were applied to all reflections, leading to a weighted R of 0.06_6. In the last refinement cycle the ratio of smallest and largest shift to standard deviation is 0.007 and 0.198, respectively. From the 555 unobserved reflections 76 were calculated to have intensities corresponding to $F_{min} < F < 3F_{min}$. The scattering factors were taken from [5](Cu), [6](O), [7](N, C_{val}), and [8](H_{bond}).

The final atomic and thermal parameters are given in Tables I and II. While Cu^{2+}, N_{11}, N_{21}, C_{13}, H_{13}, and H_{23} occupy sites with a twofold symmetry axis (8c), all other atoms are found in the 16f positions. Because no absorption correction was applied to the intensities of the plate-like crystal, the B_{33} thermal parameters are expected to be somewhat smaller with respect to B_{11} and B_{22}.

Results and Discussion

The structure of a single $Cu(terpy)_2^{2+}$ polyhedron without the hydrogen atoms of the terpyridine ligands is shown in Figure 2, the corresponding Cu–N bond distances and NCuN bond angles are listed in Table III and Figure 3. Neglecting

Table II. Anisotropic Thermal Parameters for $Cu(terpy)_2(NO_3)_2$ and Isotropic Thermal Parameters for H Atoms

Anisotropic Thermal Parameters[a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu_1	2.11 (4)	2.48 (4)	1.97 (5)	0.04 (3)	0.00	0.00
N_{11}	3.1 (3)	2.8 (3)	1.9 (2)	−0.5 (2)	0.0	0.0
N_{12}	2.2 (2)	2.3 (2)	2.6 (2)	−0.2 (2)	−0.0 (1)	0.2 (1)
C_{11}	2.7 (2)	3.3 (2)	2.0 (2)	−0.1 (2)	0.5 (2)	0.0 (2)
C_{12}	3.0 (3)	6.5 (3)	2.5 (2)	0.5 (3)	0.5 (2)	−0.0 (3)
C_{13}	4.6 (4)	7.9 (6)	2.1 (3)	0.2 (5)	0.0	0.0
C_{14}	3.1 (2)	2.5 (2)	2.5 (2)	0.2 (2)	0.9 (2)	−0.1 (2)
C_{15}	2.7 (2)	4.1 (3)	3.2 (3)	0.3 (2)	0.8 (2)	0.2 (2)
C_{16}	2.7 (2)	4.3 (3)	4.4 (3)	0.5 (2)	0.9 (2)	0.3 (3)
C_{17}	3.2 (2)	3.4 (2)	4.1 (3)	0.5 (2)	−0.4 (2)	0.2 (2)
C_{18}	3.2 (2)	3.0 (2)	3.0 (2)	−0.0 (2)	0.5 (2)	−0.3 (2)
N_{21}	2.1 (2)	3.3 (3)	1.7 (2)	−0.0 (2)	0.0	0.0
N_{22}	2.4 (2)	2.6 (2)	2.9 (2)	−0.1 (2)	0.3 (2)	−0.3 (2)
C_{21}	2.2 (2)	2.6 (2)	2.9 (2)	0.5 (2)	0.5 (2)	0.6 (2)
C_{22}	3.8 (3)	4.1 (3)	2.5 (2)	0.7 (2)	0.5 (2)	0.9 (2)
C_{23}	5.9 (5)	5.2 (5)	1.3 (3)	1.1 (4)	0.0	0.0
C_{24}	2.3 (2)	2.1 (2)	2.9 (2)	0.2 (2)	0.4 (2)	0.3 (2)
C_{25}	4.0 (3)	2.9 (2)	3.7 (3)	−0.4 (2)	0.0 (2)	0.9 (2)
C_{26}	3.9 (3)	2.6 (2)	6.1 (4)	−0.6 (2)	0.4 (3)	0.4 (3)
C_{27}	2.9 (2)	3.0 (2)	5.9 (4)	−0.6 (2)	−0.3 (3)	−1.1 (3)
C_{28}	2.6 (2)	3.3 (2)	3.4 (3)	0.1 (2)	−0.4 (2)	−0.8 (2)
N_1	4.9 (3)	5.5 (3)	2.5 (2)	0.6 (3)	0.4 (2)	0.1 (2)
O_1	4.5 (3)	9.2 (3)	5.0 (2)	1.3 (3)	−0.4 (2)	−1.3 (3)
O_2	9.0 (3)	6.8 (3)	5.7 (3)	1.6 (3)	2.8 (3)	0.4 (3)
O_3	8.5 (3)	12.5 (4)	5.0 (3)	−4.4 (4)	1.7 (3)	−2.3 (3)

Isotropic Thermal Parameters[b]

Atom	B, Å^2	Atom	B, Å^2
H_{12}	3.5 (1.5)	H_{22}	1.7 (1.4)
H_{13}	7.2 (2.0)	H_{23}	2.6 (2.0)
H_{15}	5.2 (1.4)	H_{25}	4.9 (1.4)
H_{16}	4.8 (1.4)	H_{26}	3.2 (1.4)
H_{17}	2.5 (1.4)	H_{27}	4.6 (1.4)
H_{18}	4.1 (1.4)	H_{28}	3.1 (1.5)

[a] The B_{ij}'s (Å^2) refer to the temperature factor $T = \exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hka^*c^* + 2B_{23}klb^*c^*)]$. [b] B refers to the temperature factor $T = \exp[-(B/4)((2 \sin \theta_{hkl})/\lambda)^2]$.

Table III. $Cu(terpy)_2{}^{2+}$, Bond Lengths (Å) and Bond Angles of the CuN_6 Polyhedron and the $NO_3{}^-$ Anion

$Cu-N_{11}$	1.965 (5)	$Cu-N_{21}$	2.012 (5)
$Cu-N_{12}$	2.085 (4)	$Cu-N_{22}$	2.288 (4)
$N_{11}-Cu-N_{21}$	180.0 (0)	$N_{22}-Cu-N_{22}'$	151.8 (6)
$N_{12}-Cu-N_{12}'$	157.6 (6)	$N_{12}-Cu-N_{22}$	95.6 (6)
		$N_{22}-Cu-N_{12}'$	89.9 (6)
N_1-O_1	1.215 (7)	N_1-O_2	1.223 (7)
N_1-O_3	1.234 (8)		
$O_1-N_1-O_2$	120.3 (8)	$O_2-N_1-O_3$	118.6 (8)
$O_1-N_1-O_3$	121.2 (8)		

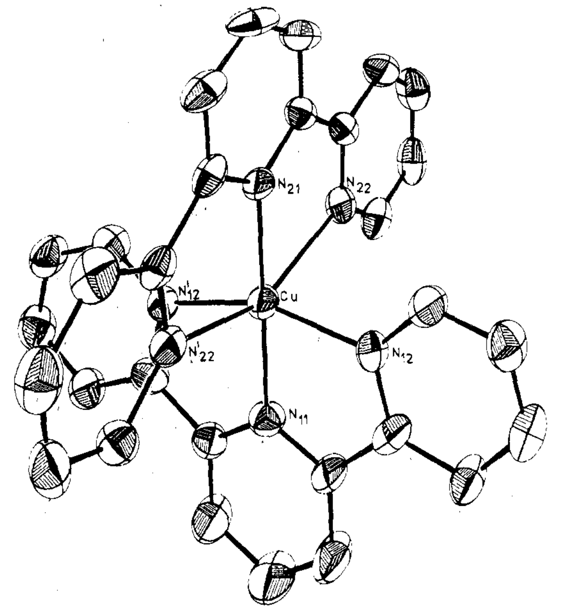

Figure 2. Structure of a $Cu(terpy)_2$ polyhedron in $Cu(terpy)_2(NO_3)_2$ (without the H atoms).

Table IV. $Cu^{2+}(terpy)_2{}^{2+}$, Root Mean Square Displacements (Å) of Cu^{2+} and the N Atoms

Cu	0.163 (3)	0.177 (3)	0.157 (4)
N_{11}	0.21 (2)	0.18 (2)	0.16 (2)
N_{12}	0.16 (1)	0.17 (1)	0.19 (1)
N_{21}	0.16 (1)	0.20 (2)	0.15 (2)
N_{22}	0.17 (1)	0.17 (1)	0.20 (1)

the nonlinear Cu–N bonds in the *uv* plane of the CuN_6 complex for the moment (Figures 1–3; $N_{12}CuN_{12'}$ = 157.6°, $N_{22}CuN_{22'}$ = 151.8°), an approximately orthorhombic distortion of the CuN_6 octahedron with bond lengths $a_w \simeq 1.99$ Å, $a_u = 2.08_5$ Å, and $a_v = 2.29$ Å and two slightly different a_w distances results. The maximal deviation of the C and N atoms of ligand 1(2) from planarity (plane equations: $4.939(-11.38)x + 11.68(5.106)y - 8.758(3.830) = 0$) is 0.057 (0.048) Å. The angle between the best planes of the two ligands thus defined deviates from 90° by $\simeq \pm 3°$. As expected the a_w bond length is the shortest one as a consequence of the rigid structure of the terpyridine ligands. The Cu^{2+} ions, however, do not adopt this compressed coordination but induce a tetragonal elongation in a bond direction perpendicular to *w*. The orthorhombic coordination can be regarded as a compromise between the "host-lattice effect"—essentially a compression along *w*—and the Jahn–Teller effect with a considerable elongation along *v* (or *u* alternatively). This geometry is feasable indeed because the $Cu(terpy)_2{}^{2+}$ cations are isolated from each other and the two ligands are nonequivalent in this particular space group. The structural behavior just discussed is a further example of the energetic preference of the elongated coordination before the compressed one, if the Jahn–Teller effect is active in octahedral Cu^{2+} complexes.[1]

The arrangement of the CuN_6 polyhedra in the unit cell is such that long (a_v) and intermediate (a_u) Cu–N bond lengths alternate in the (001) planes of the tetragonal structure in directions which are inclined to the $a(y)$ axis by 24.7° (a_v) and 21.7° (a_u), respectively (Figure 4). The directions of the short Cu–N bond lengths (a_w) are parallel to the tetragonal *c* axis. A geometric arrangement of tetragonally elongated octahedra (possibly with an orthorhombic component) is called antiferrodistortive, if the long axes of neighbored polyhedra have directions perpendicular to each other in the (001) plane. It is the most frequently observed cooperative Jahn–Teller order[1,2,9] and obviously verified in the structure under discussion also. CuN_6 polyhedra, which are displaced relative to each other by a translation of either ${}^1/_2{}^1/_20$ or $00{}^1/_2$, have the same orientation if they were rotated by 90° around the twofold axis and if a reflection with respect to the *uv* plane of the complex were applied.

The root mean square displacements of Cu^{2+} and the N atoms have normal values between 0.15 and 0.20 Å (Table IV). Furthermore, the shortest axes of the nitrogen thermal ellipsoids nearly coincide with the Cu–N bond directions (Figure 2). Both observations exclude a dynamic Jahn–Teller effect within the CuN_6 polyhedra, as it is found in the β modification of $Cs_2PbCu(NO_2)_6$ for example.[10]

The adaptation of the terpyridine rings to the pseudooctahedral geometry of the CuN_6 polyhedra gives rise to distinct

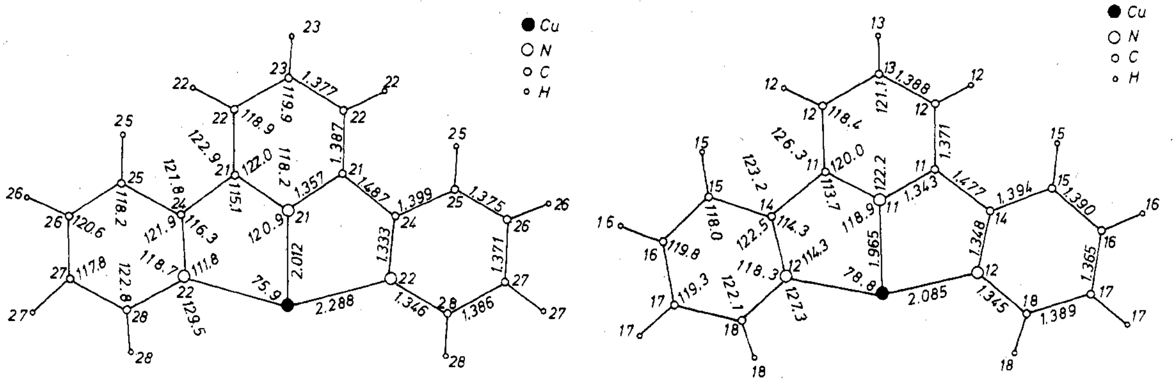

Figure 3. The geometry of the terpyridine ligands ($i = 1, 2$) bonded to Cu^{2+} in $Cu(terpy)_2{}^{2+}$. [Bond lengths and bond angles are given in the right-hand and left-hand parts of the terpyridine rings, respectively. The standard deviations for the C–C and C–N bond lengths are σ(C–C) = 0.007–0.009 Å and σ(C–N) = 0.006–0.007 Å, respectively; the angles around the ligand N and C atoms have standard deviations σ = 0.8° (compare Table III also).]

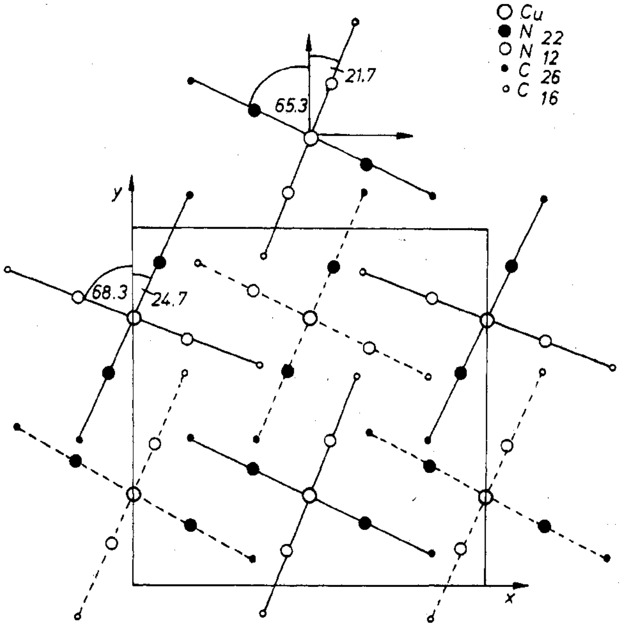

Figure 4. Projection of the CuN_6 polyhedra ($z \simeq {}^1/_8$ and ${}^3/_8$, full and broken lines, respectively) into the (001) plane. (The Cu^{2+} ions are displaced from $z = {}^1/_8, {}^3/_8$ by ±0.55 Å in the [001] directions.)

deformations of the ligand framework (Figure 3). Within the ligand rings C–C bond distances of 1.37–1.40 Å and C–N bond lengths between 1.33 and 1.36 Å are found. They are—as well as the "inner" bond angles of 120 ± 2°—still in the range of usually observed values. The "outer" $N_{i1}C_{i1}C_{i4}$ and $N_{i2}C_{i4}C_{i1}$ angles, however, are more severely influenced and squeezed to about 115°. The "tongs" of ligand 2 (115 and 116°) are further apart than those of ligand 1 (114° both), inducing shorter Cu–N_{12} bond lengths (a_u) compared to Cu–N_{22} (a_v). In addition to these ligand deformations, the CuN_6 coordination shows appreciable angular distortions. Thus, the $N_{11}CuN_{12}$ and $N_{21}CuN_{22}$ angles deviate from 90° by 11 and 14°, respectively, inducing N_{12}–$N_{12'}$ or N_{22}–$N_{22'}$ distances of 4.09 or 4.43 Å.

The NO_3^- ions are arranged in slightly staggered layers at $z = 0, {}^1/_4, {}^1/_2$, and ${}^3/_4$ between the planes of the $Cu(terpy)_2{}^{2+}$ cations (compare Figure 4). The N–O bond lengths (1.22_5 Å) are identical within the standard deviations (Table III) and the ONO angles are regular (120 ± 1°). The O atoms of the nitrate ions seem to be involved in weak C—H···O hydrogen bonds. The following configurations with H···O $\lesssim$ 2.65 Å[11] and CHO $\gtrsim$ 150° most likely represent such hydrogen bonds: C_{12}—$H_{12'}$···O_1 (2.65 Å, 160°), C_{15}—$H_{15'}$···O_1 (2.58 Å, 162°), C_{22}—$H_{22'}$···O_2 (2.49 Å, 168°), C_{25}—$H_{25'}$···O_2 (2.46 Å, 158°). H_{18} may be involved in a bifurcated hydrogen bond: C_{18}—$H_{18'}$···O_3 (2.65 Å, 120°), C_{18}—$H_{18'}$···O_1 (2.79 Å, 126°).

The single-crystal EPR investigation (35 GHz) of compounds $Cu(terpy)_2X_2 \cdot nH_2O$ (X: NO_3^-, n = 0 (I); ClO_4^-, n = 1 (II); Br^-, n = 2 (III)) yielded additional information.[3] In contrast to complex I, for which an *orthorhombic* **g** tensor with two signals in the (001) plane was found in agreement with the x-ray result presented above, the compounds II and III exhibit a *tetragonal* **g** tensor at 298 K with just one broad signal in the (001) plane. At temperatures $\lesssim$77 K the tetragonal spectrum changes into the orthorhombic spectrum, which is typical for I. Obviously the 298 K modifications of II and III exhibit dynamic behavior in the (001) plane. This "planar dynamics" may be interpreted by the following mechanism: The Cu–N bond lengths a_u and a_v fluctuate between ~2.1 and ~2.3 Å resulting in a CuN_6 coordination which is approximately tetragonally compressed *in time average*. The estimated Cu–N bond lengths for this phase are $a_z \simeq 1.9_5$–2.0 Å and $a_u' \simeq a_v' \simeq 2.1_5$–2.2 Å. A dynamical behavior of the described kind may become apparent in the root mean square displacements and alignment of the nitrogen thermal ellipsoids.[10] An x-ray structure analysis of $Cu(terpy)_2Br_2 \cdot 3H_2O$ is in progress, in order to confirm and refine the spectroscopic results. We believe that the (approximate) tetragonal compression of the CuN_6 polyhedra in II and III remaining at 298 K is essentially the kind of distortion which is forced upon the complex by the rigid structure of the terpyridine ligands alone, if a Jahn–Teller distortion is dynamic or not present. We are going to prove this suggestion by a structural analysis of $Ni(terpy)_2(NO_3)_2 \cdot nH_2O$ with a non-Jahn–Teller transition-metal ion.

The only two terpyridine complexes, the structure of which are known so far, contain low-spin Co^{2+} as central ions.[12] They are expected to behave similarly to the Cu^{2+} compounds because Co^{2+} possesses a Jahn–Teller unstable ^2E_g ground state in octahedral coordination as well.[13] The CoN_6 polyhedra are found to be tetragonally compressed in first approximation.[12] A decision as to whether a planar dynamic Jahn–Teller effect as discussed above is present is not possible from the x-ray data because the orientations and the dimensions of the thermal ellipsoids of the nitrogen atoms are not accurate enough. Our single-crystal EPR measurements on $Co(terpy)_2(NO_3)_2 \cdot nH_2O$, however, show unambigously a nearly complete analogy to the Cu^{2+} compounds.[13] At room temperature extremely broad isotropic EPR signals are obtained, which are resolved at 130 K into a spectrum which suggests a tetragonally compressed coordination in time average. This planar dynamic structure finally transforms into the static modification at $T \lesssim$ 77 K, which is characterized by an orthorhombic **g** tensor.

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Registry No. $Cu(terpy)_2(NO_3)_2$, 36300-83-1.

Supplementary Material Available: A listing of crystal structure amplitudes (9 pages). Ordering information is given on any current masthead page.

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Absolute Configurations of Organometallic Compounds. 3.[1] Structure and Absolute Configuration of the Square-Pyramidal Complex $[(+)_{579}\text{-}(C_5H_5)Mo(CO)_2(NN^*)]PF_6$ (NN* = Schiff Base Derived from Pyridine-2-carbaldehyde and (*S*)-(−)-α-Phenylethylamine)

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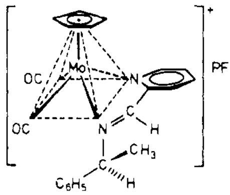
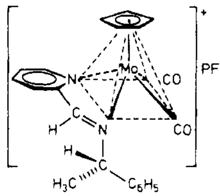
The structure of $(+)_{579}\text{-}[\eta^5\text{-}C_5H_5Mo(CO)_2(NN^*)]PF_6$ with NN* = the Schiff base derived from pyridine-2-carbaldehyde and (*S*)-(−)-α-phenylethylamine was determined using standard single-crystal x-ray diffraction methods. The absolute configuration was determined by refinement of the data using the anomalous scattering contributions of Mo and P to a final $R(F) = 0.056$ for 2634 independent reflections having $I > 3\sigma(I)$. The substance crystallizes in the space group $P2_12_12_1$ with unit cell dimensions of $a = 12.249$ (4), $b = 9.236$ (3), and $c = 20.692$ (9) Å and $Z = 4$ molecules/unit cell. The square-pyramidal coordination of the Mo atom is defined by two carbonyl carbons and two Schiff base nitrogens occupying the four basal plane sites and the five carbons of the $\eta^5\text{-}C_5H_5$ ligand in the axial position. The Mo–ligand distances and the bond lengths and angles within the ligands are normal and compare closely with those of recent structure determinations of comparable precision. The Mo atom is 0.95 Å above the plane formed by the four basal plane ligands. The conformation of the (*S*)-α-phenylethyl group with respect to the ligand plane, defined by the pyridine ring, the imine system, and the Mo atom, is discussed. The configuration at the metal atom in the $(+)_{579}$ isomer is specified as (*S*). The PF_6^- anion executes large amplitude torsional motion in the lattice, as is commonly the case for this anion when not hydrogen bonded.

Introduction

In the last 7 years, optically active organometallic compounds became available in which a transition element is the chiral center.[3,4] These stereochemically labeled compounds were used to elucidate the steric course of reactions.[5] For correlation of configuration, chiroptical and chemical methods had to be applied as the absolute configurations of all these compounds were not known. In a preliminary communication, we published the first determination of the absolute configuration of such a compound.[6] Meanwhile the determination of the absolute configurations of other optically active organometallic complexes has been announced.[2,7-9] Here we report the details of our x-ray diffraction study on the compound $(+)_{579}\text{-}[\eta^5\text{-}C_5H_5Mo(CO)_2(NN^*)]PF_6$ with NN* = Schiff base derived from pyridine-2-carbaldehyde and (*S*)-(−)-α-phenylethylamine.



A



B

In the reaction of $C_5H_5Mo(CO)_3Cl$ with the Schiff base NN* one of the carbonyl ligands and the covalently bound chlorine substituent are displaced by NN*, and in a metathetical reaction the anion Cl^- can be replaced by PF_6^-.[10,11] On substitution of CO and Cl^- in $C_5H_5Mo(CO)_3Cl$ by NN*, a new asymmetric center at the Mo atom is formed. Therefore using the (*S*)-(−)-α-phenylethyl group in the amine part of the Schiff base NN*, two diastereoisomers A and B arise which differ only in the configuration at the metal atom.[10,11] Both isomers A and B show different ^1H NMR spectra and can be separated by fractional crystallization.[11]

Compounds A and B are configurationally stable in the solid state and in solution at low temperatures. At 75 °C in DMF solution the two diastereoisomers A and B interconvert by what seems to be an intramolecular metal-centered rearrangement, probably taking place by a 180° rotation of the chelate ligand NN* with respect to the metal atom.[5,12-14] In the equilibrium at 75 °C, which in DMF is approached in a first-order reaction with a half-life of 26.3 min,[12] the isomer ratio is A/B = 40/60. This isomer ratio is a measure of the optical induction of the *S*-configurated asymmetric carbon atom in the Schiff base NN* on the formation of the two different configurations at the Mo atom in the equilibrium.[15] The asymmetric induction at the metal atom in the compounds $C_5H_5Mo(CO)_2LL^*$ is strongly dependent on the nature of the chelate ligand LL*.[15]

In the asymmetric hydrogenation of suitably substituted olefins and similar reactions the best optical yields are obtained

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