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The Crystal Structure of High-Spin Low-Spin Bis(2.2′:6′2″-terpyridyl) Co(II) Perchlorate

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Compared with iron complexes, only a few examples of high-spin low-spin behaviour in Co(II)-complexes are known. As a system of interest, we investigated the series of salts of the bisterpyridine-Co^{2+} cation, $[Co(terpy)_2]X_2\cdot nH_2O$ [1]. Recently the structure of one of these compounds with X = Br and n = 3 was determined (space group $P\bar{1}$) [2], resulting in a local symmetry of $\langle Co{-}N_6\rangle$ which corresponds approximately to a compressed octahedron. At room temperature this compound shows a magnetic moment (μ_{eff} (300 K) = 2.9 B.M.) between the two extreme values of $\mu_{eff} \cong 4.5$ for a pure quartet ground state and ≅2.0 B.M. for a pure doublet ground state. Assuming a thermal equilibrium between the two spin states, 20% of the high-spin states should be occupied with electrons at room temperature. In contrast, $[Co(terpy)_2](ClO_4)_2\cdot\frac{1}{2}H_2O$ exhibits much higher magnetic moments in the temperature range of 4.2–300 K ($\mu_{eff} \cong 4$ B.M.), thus indicating that the ratio of the two spin-state species has been shifted to a higher percentage (≃70%) of quartet ground states. Since the spin-state cross-over seems to be balanced by the lattice forces, determined mainly by the anion X and the water content n and not as usual by temperature, we investigated the structure of the magnetic high-spin d^7 $[Co(terpy)_2](ClO_4)_2\cdot\frac{1}{2}H_2O$.

The preparation of the compound has been described earlier [3]. Single crystal measurements were performed on a four-circle diffractometer (CAD4, Enraf Nonius) with graphite monochromated MoKα radiation. At 293 K, 2810 reflections were measured, of which 1291 were given zero weight ($I < 2\sigma_c(I)$). From the systematic absence of (hkl, $h + k + l = 2n$; $hk0$, $h(k) = 2n$; $00l$, $l = 4n$), the space group $I4_1/a$ (no. 88) could be deduced. The cell constants were $a = b = 12.510(2)$ Å, $c = 40.27(1)$ Å, $\alpha = \beta = \gamma = 90°$, $Z = 8$, $V = 6302(5)$ Å^3, $Dc = 1.546$ g/cm^3. The positional parameters were refined with starting values taken from the Fourier map by the conventional heavy-atom method**. Reflections were measured with the $\omega{-}2\theta$ scan technique, the scan width being defined by $\Delta\omega(°) = 0.9 + 0.353\cdot\tan\theta$ ($\theta = 2°{-}25°$). The final reliablity indices are $R = 0.078$ and $R_w = 0.072$# (with 251 parameters for the least-squares refinement). Anisotropic temperature factors were used for all atoms except H; scattering factors were those of the neutral atoms [5]. The final difference Fourier synthesis results in no peaks higher than 0.3 e/Å^3. The ClO_4^- and water molecules were found to be disordered, and the population parameters were fixed from a Fourier map. The bond distances and angles resulting from this refinement are shown in Fig. 1.† The schematic ordering of the Co-terpy-polyeders in the unit-cell is depicted in Fig. 2, by projecting the 4 different planes in the c-direction onto the *(001)*-plane.

Discussion

Each discrete $[Co(terpy)_2]^{2+}$ cation is accompanied by two ClO_4^- anions, of which three O-atoms were found at two different sites with fixed population parameters, 0.7 and 0.3. The O-atoms of the nearby water molecule also appeared to be disordered between two positions with equal populations normalized to given a total of 1. The local cation symmetry is near C_{2v}, the two planes incorporating the terpy-ligands and the c-axis forming an angle of 91.0°(5) (*cf.* Fig. 1). The crystal structure can be described by a sequence ABAB··· of staggered layers with Co-sites 0.11 Å above and below the A- and B-plane, respectively (*cf.* Fig. 1).

The average Co–N bond lengths are 0.07 Å longer in the ClO_4^-- as compared to the Br^- complex [2], in accord with the difference in ionic radii for high- and low-spin Co^{2+} ions [6]. However, optical spectra as well as single crystal EPR- and magnetic measurements (4–300 K) indicate that in the lattice two differently-oriented Co sites exist with high-spin and low-spin states [11]. In case of a thermal spin equilibrium [1] the structure deduced from the diffraction experiment should be the weighted average of the geometrically different molecules. By analogy to other structure determinations of compounds which exhibit high-spin low-spin behaviour [7],

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**A local version of the X-ray 72 system [4] adapted for the IBM 370/145 computer of the University of Marburg was used.

#$R = \Sigma|[|F_o| - |F_c|]|/|F_o|$

$R_w = \{\Sigma(|F_o| - |F_c|)^2/|F_o|^2\}^{1/2}$.

†Atomic parameters, structure factors, and anisotropic thermal parameters are available upon request.

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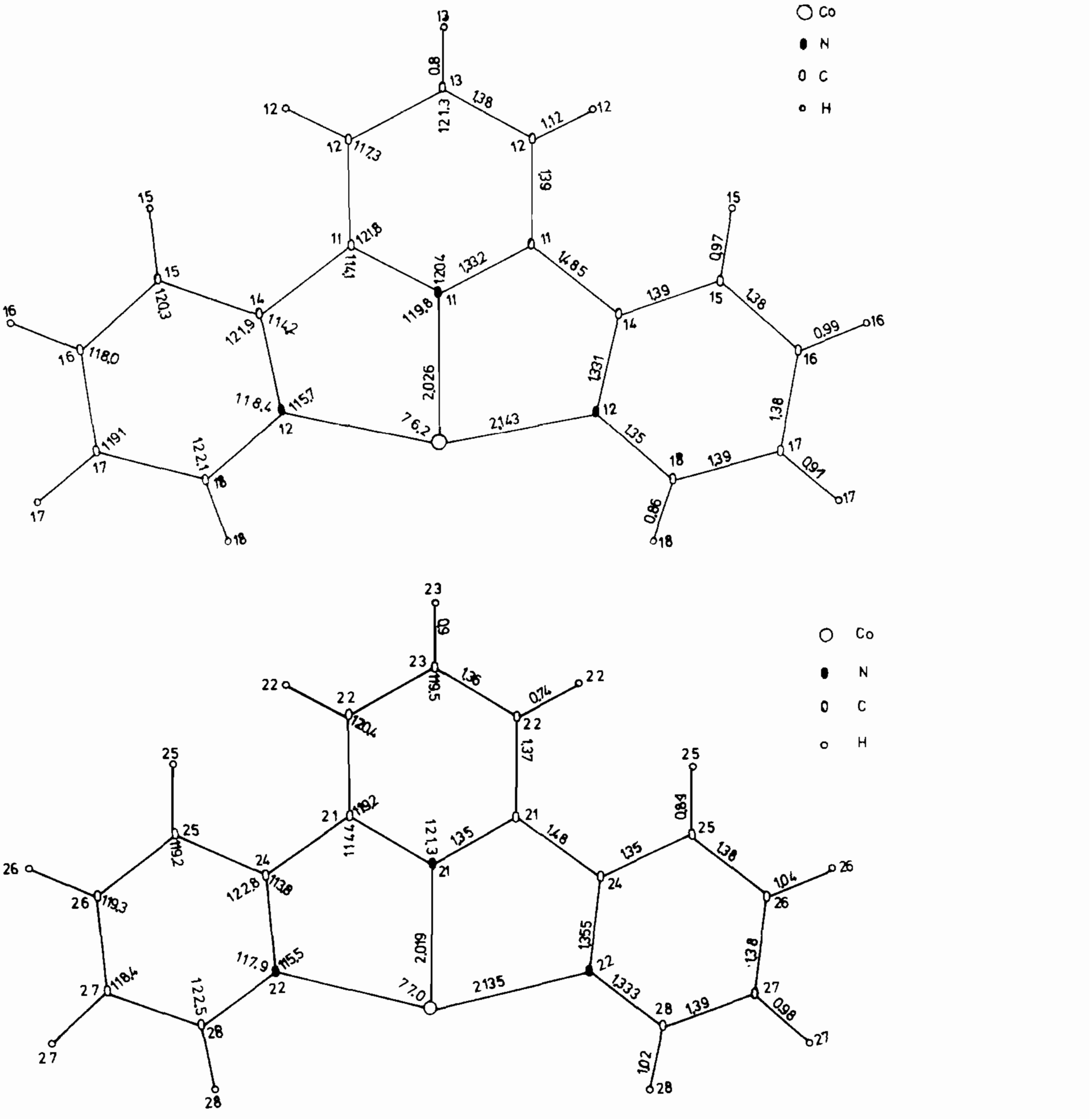

Fig. 1. The geometry of the two terpyridine ligands bonded to Co^{2+} in $[Co(terpy)_2](ClO_4)_2\cdot\frac{1}{2}H_2O$. The standard deviations for the Co–N, C–N, C–C and C–H bond lengths are 0.001–0.003 Å, 0.007–0.010 Å, 0.007–0.010 Å and 0.007–0.012 Å, respectively. The angles around the N and C atoms have standard deviations of 0.6–0.8°. The angles between the two ligands are N_{12}–Co–N_{22}: 93.9(2)° and N_{11}–Co–N_{21}: 180(0)°.

however, the corresponding disorder of the crystal could not be detected. The molecular geometries of the specific spin species can be elucidated by EPR. Analogous to $[Cu(terpy)_2](NO_3)_2$ [8], the molecular structure of the doublet state should be dynamically averaged, such that to the ligand-induced tetragonal compression in the z-axis, an elongation along the x- or y-axis due to the Jahn-Teller effect is superimposed [8]. For the high-spin states at 4.2 K, four differently oriented ⟨Co–N_6⟩ species are found (an angle of ≅35° was measured between g_{max} and the c-axes), suggesting a lower space group than $I4/a$. Thus as $\mu_{eff} \sim T$ curves do not show any sudden decrease with decreasing temperature [1], this phase transition should not be connected with an essential change of the ⟨Co–N⟩ distance or the high-spin low-spin ratio in the lattice. The molecular structure consistent with the X-ray experiment

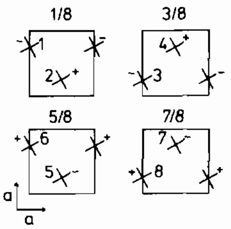

Fig. 2. The unit cell of $[Co(terpy)_2](ClO_4)_2 \cdot \frac{1}{2}H_2O$-projections of the $\langle Co-N_4 \rangle$ fragments onto the planes z = 1/8, 3/8, 5/8, 7/8. The + (–) sign designates a Co-atom 0.11 Å above (below) the plane.

at room temperature possibly exhibits dynamic superposition of the different molecular spin state geometries deduced from EPR. Compared to the Co–terpy–Br complex [2] (20% high-spin occupation), the $\langle Co-N \rangle$ distance in $[Co(terpy)_2](ClO_4) \cdot \frac{1}{2}H_2O$ (30% low-spin occupation) can be assumed to be representative for the high-spin molecules of this coordination type.

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