planar within ±0.016 Å and twisted by 4.5° about the C(2)–C(2′) bond, are consistent with those previously observed for this coordinated ligand.[17,18]

Hydrogen Bonding. The crystal packing is mainly due to a hydrogen-bond interaction between the alcoholic group and the uncoordinated carboxylate O(2) atom of an adjacent molecular unit [O(5)···O(2)^{i} = 2.668 (6) Å; O(5)–H = 0.88 Å; H···O(2)^{i} = 1.80 Å; O(5)–H···O(2)^{i} = 167.9° (i = $^{1}/_{2} - x$, $^{1}/_{2} + y$, $^{1}/_{2} - z$)]. The resulting linear chains are separated by normal van der Waals distances.

Thermogravimetric and Spectroscopic Results. The thermogravimetric analysis shows a sharp maximum in the 381–411 and 406–428 K temperature ranges, without decomposition (Table V), for the EtOH and H_2O adducts, respectively, corresponding to the complete loss of an ethanol or water molecule. That the temperature for the loss of H_2O is greater than that for the coordinated EtOH molecule strongly supports the hypothesis that the H_2O molecule is also directly involved in copper coordination.

The room-temperature solid-state electronic data and the EPR parameters at 123 K (Table V) of the aquo and the structurally known EtOH derivatives are similar, suggesting the same square-pyramidal geometry with a CuN_3O_2 chromophore for both the complexes.[14,19]

Therefore, the thermal, electronic, and EPR results confirm that the in-plane [Cu(Tsgly)(bpy)] moiety is almost unaffected by the easy replacement of ethanol with a coordinated water molecule in the apical position.

The loss of the apical ligand makes it necessary to rearrange the in-plane ligands by increasing the dihedral angle between the plane of Tsgly and bpy ligands, which gives rise to distorted tetrahedral geometry. This is supported by the shift to 14.2 × 10^3 cm^{-1} (Table V) of the d–d band maximum and the increase of g_i in the anhydrous complex with respect to those of alcoholic or aquo complexes.[20,21]

The more relevant infrared bands of our complexes are reported in Table V and are assigned by comparison with those of previously investigated copper complexes containing deprotonated *N*-tosylglycine.[2a] Table V also reports the bands attributable to coordinated ethanol and water molecules and their tentative assignments.

Acknowledgment. The authors are grateful to the Centro di Calcolo Elettronico dell'Università di Modena for computing support, the Centro Strumenti dell'Università di Modena for recording the infrared spectra, and Prof. G. C. Pellacani for the helpful discussion.

Registry No. Cu(Tsgly)(bpy)(EtOH), 88769-68-0; Cu(Tsgly)(bpy)(H_2O), 88769-67-9; Cu(Tsgly)(bpy), 88478-86-8; Cu(Tsgly)(H_2O)$_3$, 85337-92-4.

Supplementary Material Available: Listings of least-squares planes, complete bond angles and distances, hydrogen atom positions, anisotropic thermal parameters, and observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, University of Florence, Florence, Italy

Single-Crystal X-ray and Spectroscopic Studies on the Complex Aquo[tris[(3,5-dimethyl-1-pyrazolyl)methyl]amine]cobalt(II) Perchlorate. A Spectroscopic Model of Cobalt-Substituted Carbonic Anhydrase

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The X-ray structure of the complex aquo[tris[(3,5-dimethyl-1-pyrazolyl)methyl]amine]cobalt(II) perchlorate, [Co(H_2O)(MeTPMA)](ClO_4)$_2$, has been solved and shown to consist of the five-coordinate [Co(H_2O)(MeTPMA)]$^{2+}$ cation and perchlorate anions. (Crystal data: orthorhombic, space group *Pca2*$_1$, *a* = 18.456 (8) Å, *b* = 13.480 (6) Å, *c* = 10.888 (6) Å, *Z* = 4; *R* = 0.061, 1820 reflections.) The cation shows several similarities with cobalt-substituted carbonic anhydrase. The cation is essentially trigonal bipyramidal with the amino nitrogen and the water molecule in the apical positions. The electronic and EPR spectra have been measured and interpreted in terms of angular-overlap parameters.

Introduction

The complex aquo[tris[(3,5-dimethyl-1-pyrazolyl)methyl]amine]cobalt(II) perchlorate, [Co(H_2O)(MeTPMA)](ClO_4)$_2$, has been recently reported[1] to be a spectroscopic model for cobalt-substituted carbonic anhydrase (CoCA). The metal ion is coordinated by three pyrazole nitrogens, one amine nitrogen, and a water oxygen. The coordinated water in the model complex has a pK_a of 9.1, which matches with the value of CoCA in the range 6–7.5,[2] depending on the particular isoenzyme. To achieve a better understanding of the system, we have determined the X-ray structure of the above complex and have recorded its single-crystal polarized electronic and EPR spectra. In particular, it appeared interesting to us to understand the ligand field parameters of a single coordinated water molecule and investigate the possible connections with its pK_a value.

Experimental Section

Synthesis of the Complex. The complex [Co(H_2O)(MeTPMA)](ClO_4)$_2$ was prepared as reported elsewhere.[1] Crystals suitable for X-ray diffraction and polarized electronic spectra were obtained by recrystallization of the complex from ethanol–diethyl ether solutions.

X-ray Data Collection and Reduction for [Co(H_2O)(MeTPMA)](ClO_4)$_2$. The compound crystallizes in the form of elongated plates. A crystal of dimensions 0.06 × 0.20 × 0.80 mm was used for crystal data and intensity data collection. A Philips PW 1100 automatic diffractometer and graphite-monochromated MoKα radiation (λ = 0.71069 Å) were used for all operations. The lattice constants, determined from the setting angles of 12 pairs of reflections

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with $14° < \theta < 18°$, and other crystal data are as follows: orthorhombic, space group $Pca2_1$, a = 18.456 (8) Å, b = 13.480 (6) Å, c = 10.888 (6) Å, V = 2708.8 Å^3, Z = 4, M_r = 617.31, D_{calcd} = 1.513 g cm^{-3}, μ(Mo Kα) = 8.85 cm^{-1}. The intensities of 2713 independent reflections were measured in the interval $5° < 2\theta < 50°$ with a symmetric scan range of $(1.00 + 0.30 \tan \theta)°$ and a scan speed of 4°/min in 2θ. Stationary-background counts were taken at each end of the scan for a time equal to half the scan time. The intensities of three standard reflections, monitored every 120 min, showed small fluctuations (±1.5%) during the collection procedure but no systematic trend. Intensity data were corrected for Lorentz–polarization effects and for absorption (transmission coefficients ranging from 0.81 to 0.95). A total of 1820 reflections with $I > 3\sigma(I)$ were used for the structure solution and refinement. The principal computer programs used in the crystallographic calculations are listed in ref 3.

Structure Solution and Refinement for $[Co(H_2O)(MeTPMA)](ClO_4)_2$. The structure was solved by heavy-atom procedures. The position of the cobalt atom was determined from a Patterson map, and all the other non-hydrogen atoms were located in subsequent Fourier maps. Full-matrix least-squares refinement was based on minimization of the function $\sum w(|F_o| - |F_c|)^2$ with weights $w = 1/\sigma^2(F_o)$. The atomic scattering factors were taken from ref 4, and anomalous dispersion terms for the metal atom were included in F_c.[5] The z coordinate of the metal atom was fixed during the least-squares cycles due to the polar nature of the space group. One of the two ClO_4^- anions was found to be affected by rotational disorder about the chlorine atom position. In the final model for such an anion, two tetrahedral arrangements of oxygen atoms about the chlorine atom position were considered, with fixed population parameters (0.54 and 0.46, respectively, obtained from refinements in which an overall temperature factor was assigned to all oxygen atoms). The Cl–O distance and an overall temperature factor were refined for each of the two oxygen tetrahedra. In the final cycles of refinement anisotropic thermal parameters were assigned to the cobalt and chlorine atoms and to the oxygen atoms of the water molecule and of the ClO_4^- anion unaffected by disorder. The nitrogen and carbon atoms were assigned isotropic temperature factors. Hydrogen atoms were introduced in calculated positions (C–H = 1.00 Å), each with an isotropic temperature factor ca. 20% larger than that of the respective carbon atom. Methyl hydrogens were refined as a part of rigid CH_3 groups and were assigned an overall temperature factor.

Although the H_2O hydrogen atoms were not included in the final model, in a separate set of cycles an H_2O moiety was refined with the constraints that the two O–H bonds should be identical and the H–O–H angle fixed at 105°, a damping factor being also applied. The improvement in R was not significant, but in the final orientation of the H_2O group, with O–H bond lengths of 0.70 Å, the two hydrogen atoms pointed toward the oxygens of the two ClO_4^- anions. A ΔF map calculated without contributions from the H_2O hydrogen atoms showed in correspondence to their positions peaks of height ca. 0.25 e Å^{-3}. The highest peak (0.9 e Å^{-3}) in the final ΔF map lay in the region of the disordered anion. The largest shift/error ratio in the final cycle was 0.09. Convergence was attained when the values of the discrepancy indices, defined by $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$, were 0.061 and 0.062, respectively. The final positional parameters for the non-hydrogen atoms are given in Table I. Listings of thermal parameters (Tables I-S and II-S), hydrogen atom parameters (Table III-S), and observed and calculated structure amplitudes are available as supplementary material.

Electronic and EPR Spectra. The single-crystal polarized electronic spectra were recorded with a Cary 17 spectrophotometer. EPR spectra were recorded with a Varian E-9 spectrometer operating at 9 GHz and equipped with an Oxford Instruments ESR9 continuous-flow cryostat. The crystals were mounted on a Perspex rod and oriented with the aid of their geometrical features.

Results

The structure consists of $[Co(H_2O)(MeTPMA)]^{2+}$ cations and ClO_4^- anions. Figure 1 shows a perspective view of the cation. The metal atom is in a five-coordinate environment formed by three pyrazole nitrogens, by the amine nitrogen atom of the MeTPMA ligand, and by the oxygen atom of the water molecule. Values of bond distances and angles about the metal atom are listed in Table II. The coordination geometry is approximately trigonal bipyramidal with the amine nitrogen and the oxygen atom in the axial positions. The metal atom lies 0.48 Å away from the plane through the equatorial nitrogens, on the side of the oxygen atom. The rather short Co–O1 distance, of 2.024 (7) Å, is indicative of a substantial

Table I. Positional Parameters (X10^4) for $[Co(H_2O)(MeTPMA)](ClO_4)_2$[a]

atom	x	y	z
Co	-539 (1)	7893 (1)	4000
Cl1	1547 (2)	6334 (2)	1342 (4)
Cl2	-1226 (2)	8643 (2)	9960 (3)
O1	93 (4)	8143 (6)	2513 (7)
O6	-1411 (5)	7842 (7)	9190 (9)
O7	-1589 (6)	8474 (9)	11131 (10)
O8	-480 (5)	8614 (9)	10223 (10)
O9	-1420 (9)	9527 (8)	9447 (13)
O21	2272 (4)	6578 (11)	1616 (14)
O31	1183 (7)	7153 (8)	814 (14)
O41	1511 (8)	5500 (8)	559 (13)
O51	1181 (7)	6084 (11)	2472 (10)
O22	2130 (7)	6472 (14)	2189 (13)
O32	980 (7)	7015 (11)	1609 (17)
O42	1297 (9)	5344 (6)	1375 (17)
O52	1818 (9)	6548 (13)	123 (9)
N1	161 (5)	7397 (6)	5340 (8)
N2	-164 (4)	6975 (6)	6366 (8)
N3	-928 (4)	9269 (6)	4432 (7)
N4	-1364 (5)	9339 (7)	5452 (9)
N5	-1206 (4)	6825 (6)	3397 (8)
N6	-1820 (4)	6636 (5)	4103 (10)
N7	-1276 (4)	7594 (6)	5655 (8)
C1	-950 (6)	6802 (8)	6357 (11)
C2	330 (5)	6722 (8)	7212 (11)
C3	1010 (6)	6994 (7)	6755 (10)
C4	879 (6)	7398 (8)	5582 (11)
C5	126 (7)	6253 (11)	8410 (13)
C6	1404 (7)	7815 (10)	4730 (13)
C7	-1344 (6)	8530 (8)	6337 (11)
C8	-1633 (6)	10271 (8)	5592 (11)
C9	-1370 (6)	10791 (10)	4610 (11)
C10	-948 (6)	10175 (8)	3921 (14)
C11	-2117 (7)	10549 (10)	6668 (12)
C12	-566 (8)	10416 (10)	2759 (13)
C13	-1978 (5)	7296 (7)	5128 (11)
C14	-2199 (5)	5833 (7)	3681 (9)
C15	-1826 (5)	5517 (7)	2686 (10)
C16	-1224 (6)	6108 (7)	2523 (10)
C17	-2893 (6)	5498 (9)	4274 (12)
C18	-631 (6)	6007 (8)	1588 (11)

[a] Estimated standard deviations in the least significant figure(s) are in parentheses. The z coordinate of Co was not refined. The O21–O52 atoms belong to the disordered ClO_4^- anion.

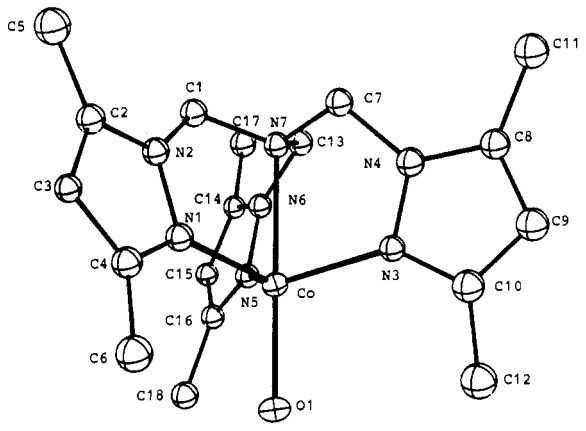

Figure 1. Perspective view of the $[Co(H_2O)(MeTPMA)]^{2+}$ cation with 20% probability ellipsoids.

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Table II. Selected Bond Lengths (Å) and Angles (deg) for $[Co(H_2O)(MeTPMA)](ClO_4)_2$[a]

Co-O1	2.024 (7)	Co-N5	2.005 (8)
Co-N1	2.060 (9)	Co-N7	2.293 (8)
Co-N3	2.044 (8)		
O1-Co-N7	178.7 (3)	N7-Co-N3	76.7 (3)
O1-Co-N1	105.0 (3)	N7-Co-N5	76.5 (3)
O1-Co-N3	103.6 (3)	N1-Co-N3	110.6 (3)
O1-Co-N5	102.2 (3)	N1-Co-N5	112.6 (3)
N7-Co-N1	76.0 (3)	N3-Co-N5	120.7 (3)

[a] Estimated standard deviations are in parentheses.

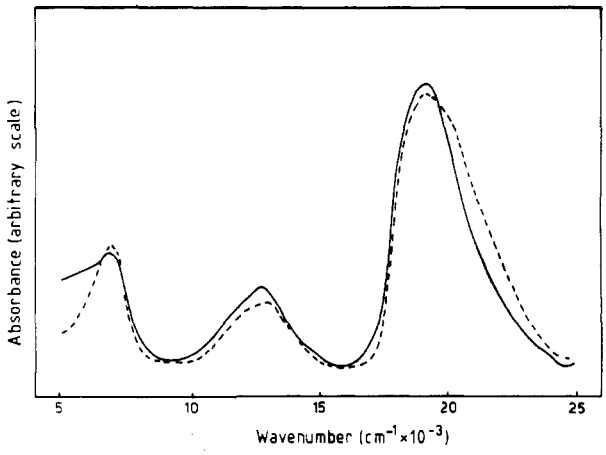

Figure 2. Single-crystal linearly polarized electronic spectra of $[Co(H_2O)(MeTPMA)](ClO_4)_2$: (—) electric vector parallel to *c*; (---) electric vector normal to *c*. The light is perpendicular to the (010) face.

metal–oxygen interaction. Such distance is indeed shorter than the 2.12 (2) and 2.102 (6) Å Co–O(H_2O) bond lengths respectively found in the high-spin five-coordinate complex aquo[*N*,*N*′-ethylenebis(3-methoxysalicylideneaminato)]cobalt(II)[6] and in the low-spin five-coordinate complex aquo-[tris[2-(diphenylphosphino)ethyl]phosphine]cobalt(II) tetrafluoroborate.[7] The present Co–O1 distance is only slightly longer than that of 1.988 (10) Å found in the Co(II) complex with cystidine 5′-monophosphate,[8] $[(C_9H_{12}N_3O_8P)Co(H_2O)]_n$, where the cobalt atom is in a tetrahedral environment of three oxygen atoms and one nitrogen atom. In the present compound there are rather close approaches to the coordinated water molecule by oxygen atoms of both perchlorate ions (O1···O32 = 2.44 Å, O1···O8 = 2.78 Å) which are indicative of hydrogen bond interactions, as also suggested by the refinement of the H_2O moiety (see Experimental Section).

Electronic Spectra. The single-crystal polarized electronic spectra were recorded on the (010) face, which is the only one suitable for this kind of experiment. The spectra, reported in Figure 2, appear as essentially unpolarized in the two orthogonal directions, owing to the fact that the *z* axis, defined as parallel to the Co–N apical bond direction, forms an angle of about 45° with the two extinction directions, which are parallel to the crystallographic *a* and *c* axes. The transitions were, therefore, assigned on the basis of comparisons with analogous spectra of high-spin trigonal-bipyramidal cobalt(II)[9] complexes and with the aid of the angular-overlap calculations described in the text. Proposed assignments (10^3 cm^{-1}): $^4A_2 \rightarrow {}^4A_2(F)$, 7.0; $^4A_2 \rightarrow {}^4E(F)$, 13.0; $^4A_2 \rightarrow {}^4E(P) + {}^4A_2(P)$, 19.3–20.2 (sh).

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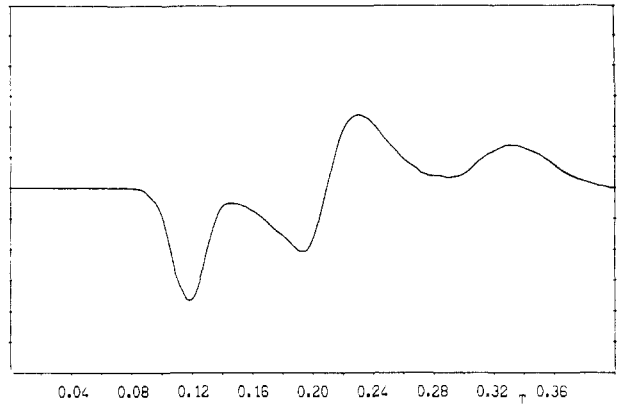

Figure 3. Polycrystalline EPR spectrum of $[Co(H_2O)(MeTPMA)](ClO_4)_2$ recorded at X-band frequency at 4.2 K in the range 0–0.4 T.

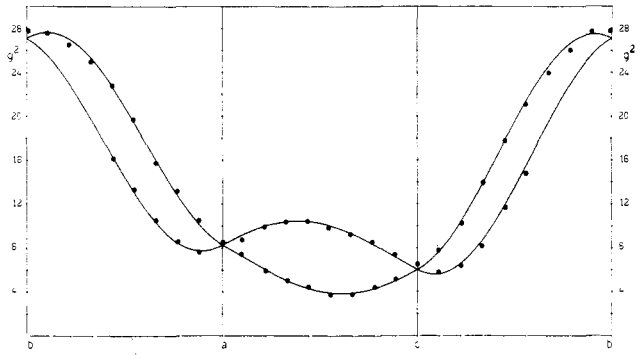

Figure 4. Angular dependence of the g^2 tensor of $[Co(H_2O)(MeTPMA)](ClO_4)_2$ in the rotation about, from left to right, the *c*, *b*, *a* crystal axes. The curves correspond to the least-squares fit to the experimental points.

Table III. Principal *g* Values and Directions for $[Co(H_2O)(MeTPMA)](ClO_4)_2$

g	crystallographic frame[a]			molecular frame[b]		
1.94 (1)	0.5570	0.0321	−0.8299	0.0077	0.1386	0.9903
3.06 (3)	−0.8111	0.2362	−0.5352	−0.9983	0.0580	−0.0003
5.33 (2)	0.1788	0.9712	0.1576	−0.0575	−0.9886	0.1387

[a] The crystallographic frame is defined as *abc*. [b] The molecular frame is centered on the metal ion with the *z* axis parallel to the metal-N_{apical} bond direction and the *x* axis parallel to a projection of the metal-N1 bond direction in the plane orthogonal to *z*.

EPR Spectra. The polycrystalline powder EPR spectrum of $[Co(H_2O)(MeTPMA)](ClO_4)_2$ recorded at 4.2 K is shown in Figure 3. The spectrum can be interpreted with an anisotropic spin Hamiltonian, with $S = {}^1/_2$ effective spin, yielding $g_1 = 1.93$, $g_2 = 3.05$, and $g_3 = 5.36$. No hyperfine splitting attributable to ^{59}Co was observed. The single-crystal spectra obtained from three orthogonal independent rotations confirm that the signals observed in the powder spectrum are associated with the same transition. The angular dependence of g^2 in the three rotations is reported in Figure 4. The principal values ($g_1 = 1.94$ (1); $g_2 = 3.06$ (3); $g_3 = 5.33$ (2)) and directions were obtained through a least-squares analysis by the Schönland method[10] and are given in Table III. The EPR spectra confirm $^4A_2$ as the ground state which is split by spin–orbit coupling into two Kramers doublets. If one assumes g_1 as $g_\parallel$ and g_2 and g_3 as the two components of a $g_\perp \sim 4.19$ split by the actual symmetry of the ligand field, lower than axial, then one may conclude that the $\pm{}^1/_2$ Kramers doublet is the ground state.[11] In fact, the smallest *g* value (1.94) was

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Table IV. Calculated[a] and Observed Electronic Transitions for $[Co(H_2O)(MeTPMA)](ClO_4)_2$

obsd[b]	calcd[b]	obsd[b]	calcd[b]
7 000	6 094	19 300	19 370
	6 658		19 414
	6 733	20 200 (sh)	19 560
	7 782		19 690
13 000	12 058		19 977
	12 209		20 054
	12 985		
	13 090		

[a] The parameters are $B = 750$ cm^{-1}, $Dq^{N_{eq}} = 1300$ cm^{-1}, $Dq^{N_{ax}} = 1050$ cm^{-1}, and $Dq^{O} = 800$ cm^{-1}. [b] All values are in cm^{-1}.

found in the *ac* plane very close (8°) to the O–Co–N_{apical} direction, with the static field at about 45° from the *a* and *c* axes. The g_2 value was found very close (16°) to the Co–N1 bond direction.

Analysis of the Spectral Data. With the aid of an angular-overlap model (AOM), developed for the d^7 high-spin configuration,[12] it is possible to reproduce both the electronic transitions and the spin-Hamiltonian parameters. The crystallographic coordinates of the donor atoms and the relative $e_\lambda(\lambda = \sigma, \pi)$ parameters, which in principle depend on the nature of the metal–ligand interaction, are the data required for the calculations.

We assume $e_\pi = 0$ for the axial amine nitrogen[13] and a π interaction orthogonal to the aromatic ring for the pyrazole nitrogen donors.[14] For the water oxygen the possibility of a π interaction with the metal ion, normal and parallel to the plane of the water molecule,[15] was considered. At a first stage, the plane was defined as passing through the donor oxygen and two oxygen atoms of the neighboring perchlorate anions.

First of all, the electronic transitions were reproduced by varying the *Dq*, defined as $^1/_{10}\,(3e_\sigma - 4e_\pi)$ and assumed equal for the three equatorial ligands, and the Racah parameter *B*. Keeping the *Dq* value for each donor atom fixed at the previously determined value, we varied the e_π/e_σ ratios to calculate the **g** tensor. Further, calculations were also performed with only the e_π/e_σ ratio for the oxygen donor being varied. In Tables IV and V the observed and calculated electronic transitions and the **g** tensor are reported together with the parameters derived from the AOM. Finally, further attempts to improve this fitting were made with different orientations of the water molecular plane: the best results were obtained within 10° from the starting position.

Table V. Best Fit of Principal *g* Values and Directions[a] [b]

	obsd	calcd		obsd	calcd
g_1	1.94 (1)	1.94	$\alpha 1$	8	8
g_2	3.06 (3)	3.09	$\alpha 2$	16	23
g_3	5.33 (2)	5.37			

[a] Parameters: $e_\sigma^{N_{eq}} = 4570$ cm^{-1}; $e_\pi^{N_{eq}} = 355$ cm^{-1}; $e_\sigma^{N_{ax}} = 3500$ cm^{-1}; $e_\sigma^{O} = 2850$ cm^{-1}; $e_{\pi\perp}^{O} = 205$ cm^{-1}; $e_{\pi\parallel}^{O} = 80$ cm^{-1}; $k = 0.84$; $\zeta = 533$ cm^{-1}. [b] α_1 is the angle between the g_1 direction and Co–N_{apical} bond direction; α_2 is the angle between the Co–N1 bond direction and g_2.

The angular-overlap parameters are in reasonable agreement with those of analogous ligands if allowance is made for differences in the metal–donor distances. The e_σ value for the equatorial nitrogens is 4550 cm^{-1}, the metal nitrogen distance being 2.05 Å, whereas it was found to be 5000 cm^{-1} in a trigonal-pyramidal compound of cobalt(II) with a ligand similar to MeTPMA and a Co–N distance of 1.94 Å.[16] The e_σ value for the apical nitrogen is the same as for the complex of $CoBr_2$ with tris[2-(dimethylamino)ethyl]amine in which the metal ion to nitrogen distance is 2.26 Å, such bond length being in the present case 2.29 Å.[11,17] Finally, the e_σ value of 3400 cm^{-1} for oxygen is consistent with the value of 2920 cm^{-1} for the hexaaquo complex, the Co–O distances being 2.02 Å for $[Co(H_2O)(MeTPMA)]^{2+}$ and 2.14 Å for $Co(H_2O)_6^{2+}$.[18,19] The Co–O bond length is smaller in the tetrahedral cobalt(II) complex mentioned previously with one coordinated water molecule (1.99 Å).[8] Presumably the e_σ value (as well as the e_π), which is proportional to the squared overlap, is even larger in that case. If the entropic factors are considered to be constant, the larger the metal–oxygen bond strength, then the lower the pK_a of coordinated water, as found for all aquo–metal complexes. Since the electronic spectra in solution of the present complex at pH <8 are substantially equal to those in the solid state,[1] it may be reasonably assumed that the spectroscopic parameters do not change from solid to solution so that they can be matched with the observed pK_a. The pK_a value of carbonic anhydrase is expected to be lower since it contains a share, more or less pronounced depending on the particular isoenzyme, of tetrahedral species.[2]

Registry No. $[Co(H_2O)(MeTMPA)](ClO_4)_2$, 76773-04-1.

Supplementary Material Available: Table I-S (anisotropic thermal parameters), Table II-S (isotropic thermal parameters), Table III-S (hydrogen atom coordinates), and listings of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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