Further work in this area will concentrate on the incorporation of thiolato groups (the origin of the blue color) and on more rigid ligand constraints, as well as on the redox properties of the resulting compounds.

Contribution from the Department of Chemistry,
Gorlaeus Laboratories, State University of Leiden, 2300 RA Leiden, The Netherlands

Synthesis and Spectroscopic Characterization of Transition-Metal Chelates Containing a New Hexadentate Ligand. Crystal and Molecular Structure of the Heptacoordinated Compound (Perchlorato-O)[N,N,N',N'-tetrakis(pyrazol-1-ylmethyl)-1,2-diaminoethane]manganese(II) Perchlorate

FRANS B. HULSBERGEN, WILLEM L. DRIESSEN,* JAN REEDIJK, and GERRIT C. VERSCHOOR

Coordination compounds of the type M(edtp)(anion)$_2$(H$_2$O)$_x$ are described in which M is one of the divalent metals Mn, Fe, Co, Ni, Cu, Zn, and Cd, the anion is ClO$_4^-$ or BF$_4^-$, edtp stands for C$_{18}$H$_{24}$N$_{10}$ or N,N,N',N'-tetrakis(pyrazol-1-yl-methyl)-1,2-diaminoethane, and x = 0–1. The compounds have been characterized by several analytical techniques and spectroscopic methods. The ligand is hexadentate in all compounds. For Mn, Fe, Cd, and Zn (in this case only for the perchlorate compound) also one counterion is coordinated to the metal ion, resulting in seven-coordination. In the case of six-coordination (M = Co, Ni, and Cu and the zinc fluoroborate compound) the coordination geometry is close to octahedral, as deduced from ligand field spectra for Co(II) and Ni(II) and powder isomorphism within this group. For Cu(II), ligand field and ESR spectra indicate a distorted octahedral geometry with parameters not largely different from those of other CuN$_6$ species. The water molecules appear to be present in the crystal lattice. The compound Mn(edtp)(ClO$_4$)$_2$ crystallizes in the space group $P2_1/c$ (monoclinic) with a = 9.522 (2) Å, b = 12.190 (6) Å, c = 22.913 (5) Å, β = 94.201 (5)°, and Z = 4. The structure was solved by heavy-atom techniques and refined by least-squares methods to a residual R value of 0.046. The coordination geometry around the Mn(II) ion can be described as derived from octahedral, with one axial donor atom replaced by two less strongly bonded donor atoms (bicapped), resulting in a seven-coordinate geometry. Apart from the six nitrogen atoms of the ligand that bind to Mn(II) (four normal distances of about 2.25 Å and two long (bicapped) distances of about 2.50 Å), an oxygen atom of one of the perchlorate ions is tightly bonded to Mn(II) (Mn–O is about 2.26 Å). In dimethylformamide solution this perchlorate ion dissociates, as deduced from conductivity data.

Introduction

As part of a research program on the synthesis and structure of coordination compounds modelling the active site in metalloproteins we have been working on tetradentate and hexadentate ligands containing imidazole groups in a more or less flexible orientation.[1–4] In these studies imidazole groups and substituted imidazole groups were selected as ligands, because they are known to occur in copper, zinc, and iron proteins.[5] Similar studies by other workers on pyridine groups held together in chelating ligands have shown that dramatic differences may occur between imidazole-containing chelates and pyridine-containing chelates.[6–8] To investigate whether or not this difference is due to steric or electronic effects, we have set up a study on the coordination chemistry of similar ligands containing pyrazole groups. The synthesis of such ligands is possible by using a new ligand-condensation technique.[9] This paper describes the first results of this investigation. As a starting ligand N,N,N',N'-tetrakis(pyrazol-1-ylmethyl)-1,2-diaminoethane, which is easily prepared from 1-(hydroxymethyl)pyrazole and ethylenediamine,[9] has been used.

To prove the chelating nature of edtp and to see to what extent all potential donor sites are involved in coordination, a crystal structure determination of a representative example has been included.

Experimental Section

The compound N,N,N',N'-tetrakis(pyrazol-1-ylmethyl)-1,2-diaminoethane (edtp) was synthesized as described before.[9]

All other chemicals were commercially available, were of sufficient purity, and were used without further treatment.

The coordination compounds were prepared by dissolving the hydrated metal salts (5 mmol) in 25 mL of ethanol and adding the warm (ca. 60 °C) solutions to warm solutions of the ligand edtp (5 mmol) in 25 mL of ethanol. After the mixtures were allowed to stand at

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(2) Birker, P. J. M. W. L.; Hendriks, H. M. J.; Reedijk, J.; Verschoor, G. C. *Inorg. Chem.* **1981**, *20*, 2408.
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(4) Birker, P. J. M. W. L.; Helder, J.; Henkel, G.; Krebs, B.; Reedijk, J. *Inorg. Chem.* **1982**, *21*, 357.
(5) Ibers, J. A.; Holm, R. H. *Science (Washington, D.C.)* **1980**, *209*, 223.
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(9) Driessen, W. L. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 441.

room temperature, in some cases only after evaporation of part of the solvent on a rotatory evaporator or after addition of some diethyl ether, solid compounds formed that were collected on a glass filter, washed once with a small portion of cold ethanol and once with a small portion of diethyl ether, and dried at 30 °C (200 mmHg). Recrystallization from absolute ethanol rendered single crystals suitable for X-ray crystallography only for the Mn–perchlorate compound.

Metal analyses were carried out complexometrically with EDTA as the complexing agent.[10] C, H, and N analyses were carried out by Dr. F. Pascher, Bonn, FRG.

Infrared spectra in the 4000–300-cm^{-1} range of the samples mulled in Nujol between KRS-5 disks or pelleted in KBr and far-infrared spectra in the 400–200-cm^{-1} range of the samples pelleted in powdered polyethylene with a polyethylene pellet as reference were recorded on a Perkin-Elmer 580 spectrophotometer equipped with a PE infrared data station.

Solid-state electronic spectra (28 000–5000 cm^{-1}) were recorded on a Beckman DK-2A spectrophotometer fitted with a reflectance attachment, using MgO as a reference.

Electron spin resonance spectra of the powdered copper compounds were obtained with a Varian E-3 spectrophotometer at X-band frequencies at room temperature and at 77 K (liquid nitrogen).

The conductivity of 10^{-3} M solutions in nitromethane (κ = 5.4 × 10^{-6} cm^{-1} Ω^{-1}) was measured at 20 °C on a Seybold type LTB conductometer.

Proton nuclear magnetic resonance spectra were recorded on a JEOL PS-100 instrument employing a frequency of 99.5 MHz, using Me$_4$Si as internal standard.

X-ray powder diagrams of the compounds were obtained with a Guinier type powder camera, using Cu Kα radiation. The samples were protected from atmospheric vapor by adhesive tape.

Mössbauer measurements were performed by Dr. A. M. van der Kraan (Interuniversity Reactor Institute) on a constant-acceleration spectrophotometer mounted with a 25 mCi of ^{57}Co source diffused into a 10-μm palladium foil. The correlation of the source to the sodium nitroprusside standard is 0.45 mm/s.

Crystal Data: C$_{18}$H$_{24}$Cl$_2$MnN$_{10}$O$_8$, mol wt 634.40, monoclinic, space group $P2_1/c$, a = 9.522 (2) Å, b = 12.190 (6) Å, c = 22.913 (5) Å, β = 94.201 (5)°, V = 2659.4 (8) Å^3, Z = 4, d_{calcd} = 1.62 g cm^{-3}, d_{measd}(flotation) = 1.63 g cm^{-3}, $F(000)$ = 1302.46, μ(Mo Kα) = 7.47 cm^{-1}, λ(Mo Kα) = 0.710 73 Å.

Data Collection and Structure Refinement. A single crystal of approximate dimensions 0.48 × 0.20 × 0.05 mm, mounted in a glass capillary, was used for data collection. Cell dimensions were determined by least-squares refinement of the measured setting angles of 24 reflections (10 < θ < 12°). The diffraction data were collected at room temperature on an Enraf-Nonius CAD-4 computer-controlled four-circle diffractometer using graphite-monochromatized Mo Kα radiation by the ω–θ scan technique for 2 ≤ θ ≤ 24° with –10 ≤ h ≤ 10, 0 ≤ k ≤ 13, and 0 ≤ l ≤ 26.

In total, 4267 reflections were measured, of which 4149 were independent; from these independent reflections there were 1855 reflections, with $I > 2\sigma(I)$, considered as observed and used in the refinement. Intensities were corrected for Lorentz and polarization effects. Absorption correction was not necessary. The calculations were performed on the Leiden University Amdahl V7B and IBM 370/158 computers using a local set of computer programs. Scattering factors and anomalous dispersion corrections were taken from ref 11. The structure was solved by the heavy-atom technique and refined by full-matrix least-squares calculations. Hydrogen atoms with fixed isotropic thermal factors of 4.0 Å^2 were placed at distances of 0.93 Å from the parent atoms. The thermal parameters of the non-hydrogen atoms were anisotropically refined. The function minimized was $\Sigma w||F_o| - |F_c||^2$ with w = 1. At the final stage the conventional discrepancy index R_f had been reduced to 0.046 (R_f = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$).

For the non-hydrogen atoms the atomic coordinates and the isotropic thermal parameter are listed in Table I. Bond distances are given in Table II and bond angles in Table III. The numbering scheme of the ligand is given in Figure 1, and the molecular entity [Mn-(edtp)(ClO$_4$)]$^+$ is depicted in Figure 2. Lists of the atomic coordinates

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(11) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England 1974; Vol. IV.

Table I. Fractional Coordinates (×10^4) and Isotropic Thermal Factors (Å^2) of the Non-Hydrogen Atoms of Mn(edtp)(ClO$_4$)$_2$

	x/a	y/b	z/c	B_{iso}^{a}
Mn	4084 (1)	2977 (1)	1308 (1)	3.03 (3)
N(1)	1935 (6)	3869 (5)	833 (3)	3.2 (2)
N(2)	2200 (6)	1551 (5)	1138 (3)	3.7 (2)
C(3)	913 (7)	3042 (8)	582 (3)	4.2 (2)
C(4)	799 (8)	2071 (8)	983 (3)	4.3 (3)
C(5)	2393 (8)	4562 (6)	369 (4)	4.3 (3)
N(11)	3454 (7)	3976 (5)	65 (3)	3.6 (2)
N(12)	4475 (7)	3446 (5)	397 (3)	3.5 (2)
C(13)	5313 (8)	3060 (7)	2 (4)	4.4 (3)
C(14)	4877 (10)	3375 (7)	–555 (4)	5.1 (3)
C(15)	3685 (10)	3951 (7)	–504 (4)	4.6 (3)
C(7)	1363 (8)	4516 (7)	1295 (4)	4.1 (3)
N(21)	2516 (6)	5125 (5)	1601 (3)	3.6 (2)
N(22)	3826 (6)	4685 (5)	1649 (3)	3.6 (2)
C(23)	4595 (8)	5420 (7)	1978 (4)	4.2 (3)
C(24)	3775 (10)	6292 (8)	2131 (4)	5.3 (3)
C(25)	2476 (9)	6100 (7)	1875 (4)	4.3 (3)
C(6)	2701 (9)	874 (7)	676 (4)	4.9 (3)
N(31)	4148 (8)	577 (6)	816 (3)	4.0 (2)
N(32)	5043 (7)	1332 (5)	1068 (3)	4.0 (2)
C(33)	6266 (9)	812 (8)	1123 (4)	5.1 (3)
C(34)	6162 (10)	–246 (9)	915 (4)	6.1 (4)
C(35)	4803 (13)	–372 (8)	724 (4)	5.8 (4)
C(8)	2165 (10)	907 (7)	1688 (4)	5.6 (3)
N(41)	2259 (7)	1727 (6)	2169 (3)	4.4 (2)
N(42)	3215 (7)	2536 (6)	2165 (3)	4.3 (2)
C(43)	3033 (9)	3062 (8)	2663 (4)	5.8 (3)
C(44)	2040 (11)	2606 (10)	2972 (4)	6.8 (4)
C(45)	1540 (9)	1745 (9)	2649 (4)	6.4 (4)
Cl(1)	–698 (3)	3029 (2)	4237 (1)	5.3 (1)
O(1)	–154 (9)	1971 (6)	4157 (3)	10.3 (3)
O(2)	–1614 (7)	3014 (8)	4665 (4)	13.2 (4)
O(3)	–1321 (9)	3440 (6)	3716 (3)	11.2 (3)
O(4)	414 (9)	3673 (7)	4424 (4)	12.1 (4)
Cl(2)	7662 (2)	3501 (2)	1759 (1)	5.6 (1)
O(21)	8555 (6)	2653 (6)	1952 (3)	7.8 (2)
O(22)	6246 (5)	3230 (4)	1766 (3)	5.9 (2)
O(23)	7856 (9)	3675 (10)	1172 (5)	17.3 (5)
O(24)	7967 (9)	4434 (9)	2039 (7)	22.1 (7)

^{a} B_{iso} = $^8/_3\pi^2$(trace $\tilde{U}$).

Table II. Some Interatomic Distances (Å) for Mn(edtp)(ClO$_4$)$_2$ with Their Estimated Standard Deviations in Parentheses

Mn–N(1)	2.496 (6)	Mn–N(2)	2.508 (6)
Mn–N(12)	2.223 (6)	Mn–N(22)	2.243 (6)
Mn–N(32)	2.287 (7)	Mn–N(42)	2.252 (7)
Mn–O(22)	2.262 (5)	C(3)–C(4)	1.506 (10)
C(3)–N(1)	1.487 (9)	C(4)–N(2)	1.497 (9)

Table III. Some Bond Angles (deg) for Mn(edtp)(ClO$_4$)$_2$

O(22)–Mn–N(1)	146.3 (2)	O(22)–Mn–N(2)	141.5 (2)
O(22)–Mn–N(12)	101.0 (2)	O(22)–Mn–N(32)	82.2 (2)
O(22)–Mn–N(22)	80.3 (2)	O(22)–Mn–N(42)	90.5 (2)
N(1)–Mn–N(12)	70.5 (2)	N(2)–Mn–N(12)	101.5 (2)
N(1)–Mn–N(22)	68.9 (2)	N(2)–Mn–N(22)	127.0 (2)
N(1)–Mn–N(32)	127.3 (2)	N(2)–Mn–N(32)	69.4 (2)
N(1)–Mn–N(42)	98.2 (2)	N(2)–Mn–N(42)	70.4 (2)
N(12)–Mn–N(22)	96.8 (2)	N(22)–Mn–N(32)	162.4 (3)
N(12)–Mn–N(32)	84.4 (2)	N(22)–Mn–N(42)	82.0 (2)
N(12)–Mn–N(42)	168.1 (2)	N(32)–Mn–N(42)	100.3 (2)
N(1)–Mn–N(2)	70.4 (2)	Mn–O(22)–Cl(2)	151.5 (4)
Mn–N(1)–C(3)	111.5 (5)	Mn–N(2)–C(4)	111.0 (5)
Mn–N(1)–C(5)	117.0 (4)	Mn–N(2)–C(6)	103.7 (4)
Mn–N(1)–C(7)	104.9 (4)	Mn–N(2)–C(8)	107.2 (5)
Mn–N(12)–N(11)	119.1 (5)	Mn–N(32)–N(31)	116.7 (5)
Mn–N(12)–C(13)	134.1 (6)	Mn–N(32)–C(33)	139.5 (7)
Mn–N(22)–N(21)	117.6 (5)	Mn–N(42)–N(41)	118.3 (5)
Mn–N(22)–C(33)	137.8 (6)	Mn–N(42)–C(43)	135.4 (7)

of the hydrogen atoms, of the anisotropic thermal parameters of the non-hydrogen atoms, and of the observed and calculated structure factors are available as supplementary material.[12]

(12) Supplementary material.

Table IV. Colors, X-ray and Infrared Type, Electronic Absorption, and Coordination Number of the Coordination Compounds of the Ligand edtp

	X-ray type[a]	IR type	color	electronic abs (powder reflctnce)[b]	coord no.
$Mn(edtp)(ClO_4)_2$	A	I	white		7
$Mn(edtp)(BF_4)_2$	A	I	white		7
$Fe(edtp)(ClO_4)_2 \cdot H_2O$	A'	I'	cream	10.9	7
$Fe(edtp)(BF_4)_2 \cdot H_2O$	A''	I'	cream	11.5	7
$Cd(edtp)(ClO_4)_2 \cdot H_2O$	A'	I'	white		7
$Cd(edtp)(BF_4)_2 \cdot H_2O$	A'	I''	white		7
$Zn(edtp)(ClO_4)_2 \cdot H_2O$	A''	I	white		7
$Zn(edtp)(BF_4)_2$	B	II	white		6
$Co(edtp)(ClO_4)_2 \cdot H_2O$	B	II	orange-red	10.2,[c] 21.5	6
$Co(edtp)(BF_4)_2 \cdot H_2O$	B	II	brown-red	10.2,[c] 21.3	6
$Ni(edtp)(ClO_4)_2 \cdot H_2O$	B	II	purple	11.1, 18.3, 28.6	6
$Ni(edtp)(BF_4)_2 \cdot H_2O$	B	II	purple	11.4, 18.9, 29.4	6
$Cu(edtp)(ClO_4)_2 \cdot H_2O$	C	III	blue	14.9 (9.9 sh)	6
$Cu(edtp)(BF_4)_2 \cdot H_2O$	D	IV	blue	15.2 (11.1 sh)	6

[a] Structural isomorphism based on powder diffraction patterns (the primes denote very slight differences). [b] Frequencies in 10^3 cm^{-1}. [c] Broad asymmetric band; sh = shoulder.

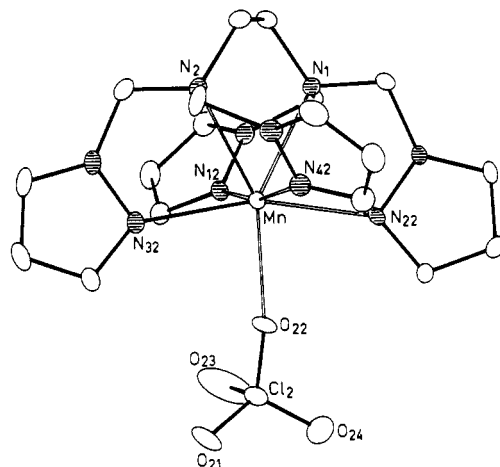**Table V.** Mössbauer Data of the Iron(II) edtp Compounds[a]

	300 K		77 K		4.2 K	
	IS	QS	IS	QS	IS	QS
$Fe(edtp)(ClO_4)_2$	1.37	2.99	1.51	3.36	1.52	3.40
$Fe(edtp)(BF_4)_2$	1.34	2.67	1.47	3.17	1.47	3.27

[a] Isomer shift (IS) and quadrupole splitting (QS) in mm s^{-1}, relative to the NBS standard, $Na_2Fe(CN)_5NO \cdot 2H_2O$.
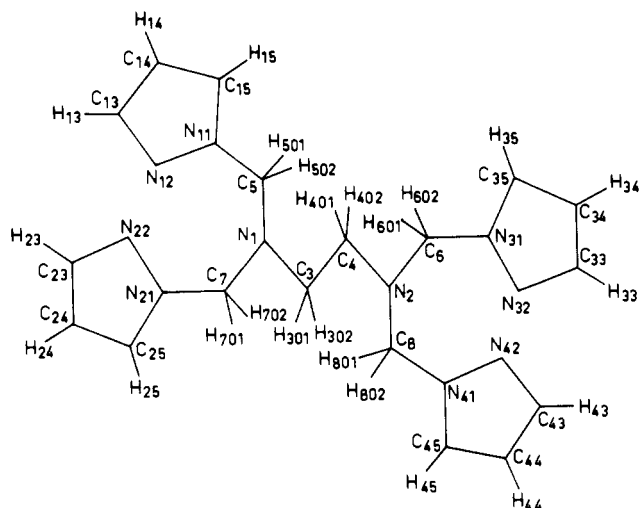
Figure 1. Atomic numbering of the ligand edtp, adopted for the description of the structure of [Mn(edtp)(ClO₄)](ClO₄).

Figure 2. ORTEP projection of the molecular entity [Mn(edtp)(ClO₄)]⁺. The hydrogen atoms are omitted.

Results and Discussion

General. Colors, X-ray diffraction type, and spectroscopic information of the new compounds are given in Tables IV–VI. All compounds gave satisfactory elemental analyses (analytical data are available as supplementary material[12]). The infrared spectra are characteristic in many detail for pyrazole derivatives and for the respective anions. When they are observed in greater detail, it appears that the infrared spectra of the

edtp compounds with manganese, iron, and cadmium perchlorates and fluoborates and zinc perchlorate are very similar. Observed differences are very slight and are indicated by the primes. The same holds for the edtp compounds with cobalt and nickel perchlorates and fluoborates and zinc fluoborate. This "infrared isomorphism" agrees very nicely with the structural isomorphism based on the X-ray powder diffraction measurements (see Table IV). The copper compounds appear to be not isomorphous according to their X-ray powder patterns and their infrared spectra (see Table IV). On the other hand, ligand field and ESR spectra of the copper compounds indicate the direct surroundings of the copper ions to be very similar (vide infra).

Description of the Structure of [Mn(edtp)(ClO₄)](ClO₄). The manganese(II) ion is surrounded by six nitrogens and one oxygen (see Figure 2). The oxygen stems from one of the two perchlorate anions. The nitrogen atoms originate from the ligand edtp, which utilizes in this way its maximum number of donor sites, viz. four pyrazole nitrogens and two tertiary

Table VI. ESR Parameters of the Copper edtp Compounds and of Copper Dopes in the Cadmium and Zinc edtp Compounds

	temp	$g_\perp$	$A_\perp(SHF)^a$	$g_\parallel$	$A_\parallel(HF)^a$	$A_\parallel(SHF)^a$
$Cu(edtp)(ClO_4)_2 \cdot H_2O$	room	2.10		2.24		
$Cu(edtp)(BF_4)_2 \cdot H_2O$	room	2.09		2.26		
$Zn(edtp)(ClO_4)_2 \cdot H_2O$	liquid N_2	2.10		2.28	137	
$Zn(edtp)(BF_4)_2 \cdot H_2O$	room	2.09		2.26	121	
$Cd(edtp)(ClO_4)_2 \cdot H_2O$	liquid N_2	2.07	13.0	2.34	160	12.3
$Cd(edtp)(BF_4)_2 \cdot H_2O$	liquid N_2	2.06	12.7	2.33	152	12.1

[a] Values in 10^{-4} cm^{-1}. HF = hyperfine splittings; SHF = superhyperfine splittings.

amine nitrogens. The four pyrazole nitrogens lie in a more or less reactangular arrangement around the Mn ion. Together with the oxygen atom O(22) they form five of the six vertices of an octahedron. When it is viewed in this way at the direct environment of the manganese ion, it is only logical to consider the apex of the octahedron to be formed by the two tertiary nitrogen atoms together. Therefore, the coordination geometry around the central metal ion can best be described as bicapped octahedral. That this description is a justified one can be seen from the lengths of the manganese to donor atom bonds: The lengths of the bonds from the manganese ion to the oxygen atom O(22) and to the nitrogen atoms N(12), N(22), N(32), and N(42), which range from 2.22 to 2.29 Å (see Table II), can be regarded as normal for octahedral Mn(II). The distances of the Mn(II) ion to the tertiary nitrogen atoms N(1) and N(2), which are about 2.50 Å, can be regarded as unusual. They are significantly longer than normal, although lying well within the bonding limit.

This rather unusual configuration can be attributed to the size of the metal ion and the limited flexibility of the ligand: The coordination angles formed between the bonds from manganese to the tertiary amine nitrogen on the one hand and the bonds from manganese to the pyrazole nitrogens on the other hand are significantly smaller than 90°, as is the coordination angle between the N(1) to Mn and N(2) to Mn bonds (see Table III). Accomodation of these angles to 90°, octahedral coordination angles, would impose severe strain on the five 5-membered rings formed by the ligand and the central metal ion and, consequently, on the ligand itself.

Coordination geometries similar to the one found in the present compound have been reported.[2,13] Bicapped coordinations have been described with ligands that, like edtp, can be considered as derived from ethylenediamine, viz. ethylenediaminetetraacetic acid (EDTA)[13] and N,N,N',N'-tetrakis(benzimidazol-2-ylmethyl)ethylenediamine ($C_{34}H_{32}N_{10}$ = edtb).[2] X-ray structural analysis[13] of $[M(EDTA)(H_2O)]^{2-}$, with M as Mg or Mn, shows a seven-coordinate N_2O_5 environment of the metal ion similar to the seven-coordinate N_6O environment in $[Mn(edtp)(ClO_4)]^+$: Four oxygens of the four acetate groups constitute, together with the oxygen of the water molecule, the five vertices of an octahedron, the apex of the octahedron being occupied by the amine nitrogens. The X-ray structural analysis[2] of $[Cu(edtb)]^{2+}$ shows a six-coordinate N_6 environment of the copper ion in a bicapped square-pyramidal geometry. In this case the underside of the copper ion is shielded by the phenyl groups of the ligand, which prevents a seventh donor to approach the central metal ion.

The pyrazole rings of the ligand in $[Mn(edtp)(ClO_4)]ClO_4$ are planar, with normal bond lengths and angles.[12] The packing of the coordination units and the anions in the crystal lattice proceeds through normal van der Waals contacts. Conductance measurements of this compound dissolved in dimethylformamide reveals that this compound is a 1:2 electrolyte in 10^{-3} M solution ($\lambda = 151$ Ω^{-1} mol^{-1} cm^2). Apparently the perchlorate anion, which is coordinated to the manganese ion in the solid state, dissociates in solution and is replaced, probably, by a solvent molecule.

The infrared spectrum of $Mn(edtp)(ClO_4)_2$ indicates the presence of some water, although this must be less than one water molecule per formula unit, as indicated by the elemental analyses. The water molecules could not be located in the Fourier map. Assumedly, they are disordered in holes near the anions.

Spectroscopic Results. To obtain further information about the coordination geometry of the other compounds and the chelating properties of edtp, the spectroscopic properties were investigated in some detail. In Table V the Mössbauer data of the iron compounds of edtp are given. The values for the isomer shifts fall in the range that is normal for high-spin divalent iron complexes with a high coordination number.[14] The value for the quadrupole splitting parameter is rather large and increases on cooling. These observations indicate a significant departure from cubic symmetry around the iron(II) ions. This is in agreement with the proposed bicapped "octahedral" N_6O coordination (by isomorphism with the Mn compound; see Table IV). The Mössbauer spectrum of the iron(II) compound of a related ligand, viz. $Fe(tpen)(ClO_4)_2$ with tpen being the pyridine analogon of edtp, revealed the iron(II) to be low spin and in a noncubic environment.[8] This dramatic difference must be due to a combination of electronic and steric effects, as the ligands edtp and tpen resemble each other very much, at least as far as the relative positions of the donor atoms are concerned. The electronic spectra of the present two iron compounds (see Table IV) are indicative for high-spin Fe^{2+}.

Position and shape of the absorption band in the diffuse reflectance spectra of the copper complexes (see Table IV) indicate a tetragonally distorted environment of the Cu(II) ions. The ESR powder spectra of the copper compounds also show the copper ions to be in an "elongated octahedral" ($d_{x^2-y^2}$ ground-state) environment of six nitrogen donor atoms (see Table VI). The presence of a weak signal at half-field ($g \approx 4.3$) indicates some cooperative effect between the copper ions. The fact that no hyperfine interactions are observed indicates that the Cu^{2+} ions are rather close together in the lattice, giving rise to so-called exchange-narrowed signals.[15] Therefore, dopes of Cu^{2+} in the lattices of the corresponding Cd and Zn compounds were studied (see Table VI). Isolated copper(II) species are present in these host lattices, now allowing the observation of even superhyperfine splittings. The parameters agree with a square-based coordination geometry of a CuN_4 chromophore.[15] The two X-ray types (Table IV) result in two different ESR spectra. The spectrum of the $Zn(ClO_4)_2$ compound, however, has slightly different parameters, compared to the Cd compounds, probably resulting from a smaller ionic radius.

The electronic absorption spectra of the cobalt and nickel compounds reveal that these metal ions are hexacoordinated in a fashion that is close to octahedral.[16-18] The rather broad first band in the diffuse reflectance spectrum (see Table IV) of the cobalt compounds indicates that the direct environment of the cobalt ions deviates somewhat from a regular octahedron. However, the ligand field parameters calculated from the positions of the absorption bands, $Dq = 1115$ cm^{-1} and $B = 835$ cm^{-1} for $Co(edtp)(ClO_4)_2$ and $Dq = 1115$ cm^{-1} and $B = 820$ cm^{-1} for $Co(edtp)(BF_4)_2$, lie in the range normally observed for an octahedral N_6 chromophore.[17] Shapes and positions of the electronic absorption bands in the spectra of the nickel compounds reveal a quite regular octahedral environment for the nickel ions. The calculated ligand field parameters, $Dq = 1110$ cm^{-1} and $B = 865$ cm^{-1} for $Ni(edtp)(ClO_4)_2$ and $Dq = 1140$ cm^{-1} and $B = 890$ cm^{-1} for $Ni(edtp)(BF_4)_2$, are in agreement with an octahedral N_6 chromophore.[18] The more or less regular octahedral coordination geometry of the cobalt and nickel compounds must

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originate from their small ionic radius. The ligand edtp is able apparently to fold itself almost optimally around the nickel and cobalt ions. With the larger metal ions (Fe, Mn, and Cd) six-coordinate octahedral coordination by the ligand edtp becomes too unfavorable, even when distorted, resulting in seven-coordinate "bicapped octahedral" geometries around the metal ions. The zinc compounds appear to be intermediate cases (see the coordination numbers in Table IV).

Concluding Remarks. The pyrazole derivative of ethylenediamine, edtp, appears to be a hexadentate nitrogen donor ligand toward first-row transition-metal ions. Except for the small nickel(II) ion the ligand edtp has a too restricted geometrical configuration to be able to form regular coordination octahedrons. Coordination numbers show a direct correlation with the ionic radii of the metal ions: The larger ions are seven-coordinate and the smaller ions are six-coordinate with Zn(II) in an intermediate position.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding,
Texas A&M University, College Station, Texas 77843

Further Studies of the Phosphine Complexes of Niobium(IV) Chloride

F. ALBERT COTTON,* STAN A. DURAJ, and WIESLAW J. ROTH

Three compounds of empirical formula NbCl$_4$(PR$_3$)$_2$, two of which (1 and 2) were previously reported and one of which (3) is new, have been structurally characterized. Compound 1, Nb$_2$Cl$_8$(PMe$_3$)$_4$, is dinuclear, consisting of two square-antiprismatic NbCl$_6$(PMe$_3$)$_2$ units fused on a common square face formed by four Cl atoms. The molecule has crystallographic *mmm* (D_{2h}) symmetry in the cubic space group *Im*3 with a = 16.372 [4] Å and Z = 6. The Nb–Nb distance is 2.833 (1) Å and the metal to ligand distances are Nb–Cl$_b$ = 2.541 (1) Å, Nb–Cl$_t$ = 2.502 (1) Å, and Nb–P = 2.671 (1) Å. Compound 2, *trans*-NbCl$_4$(PEt$_3$)$_2$, forms monoclinic crystals (*P*2$_1$/*n*) with unit cell dimensions of a = 7.224 (2) Å, b = 12.131 (4) Å, c = 12.017 (2) Å, β = 90.74 (2)°, and Z = 2. Compound 3, *trans*-NbCl$_4$(PEtPh$_2$)$_2$, also forms monoclinic crystals (*P*2$_1$/*n*) with a = 9.851 (2) Å, b = 16.010 (3) Å, c = 9.367 (2) Å, β = 98.67 (1)°, and Z = 2. In both 2 and 3 there is crystallographic inversion symmetry imposed on the molecule, and the mean dimensions (for 2 and 3 in that order) are Nb–Cl = 2.366 [9], 2.367 [34] Å and Nb–P = 2.664 (3), 2.706 (1) Å. Observations on the colors, visible spectra, and EPR spectra of solutions of these compounds are reported and partially interpreted. Compound 1 and the previously reported Nb$_2$Cl$_8$(PMe$_2$Ph)$_4$ exist in concentration-dependent equilibrium with EPR-active monomers, although the exact nature of the latter is uncertain.

Introduction

Our knowledge of the fundamental chemistry of the elements niobium and tantalum still has surprising lacunae. One of these is in the area of the phosphine adducts of the tri- and tetrahalides.[1–4] The existence of the compounds has been recognized since at least 1976,[2] but information on their molecular structures, bonding, or chemical behavior is very incomplete. A program in this laboratory to explore new areas in the chemistry of these elements has brought us to the realization that we are often lacking the kind of basic information on which we wish to build. With regard to the chemistry of "simple" phosphine adducts, we decided to remedy this need ourselves. Happily, we have found that the subject is intrinsically quite interesting since the behavior of some of these compounds is not at all "simple".

In this paper we are concerned only with some bis(phosphine) adducts of niobium(IV) chloride, "NbCl$_4$(PR$_3$)$_2$". Manzer[2] reported those with PEt$_3$ and PMe$_3$ in 1977 as orange or brown solids. He also reported that "NbCl$_4$(PMe$_3$)$_2$" had a μ_{eff} value at room temperature of only 0.50 μ_B. Samuel and co-workers[3] have reported the EPR spectra of the compounds with R = butyl, isobutyl, and ethyl in both fluid and frozen solutions. They found all three compounds to have similar spectra and argued that the only reasonable interpretation of these required the assumption of trans structures with a spin Hamiltonian based on D_{4h} symmetry. While their argument was plausible, it did not seem to us to be conclusive, and moreover, we had observed puzzling color changes with other compounds of this class on going from solid to solution. Furthermore, Manzer's magnetic data for NbCl$_4$(PMe$_3$)$_2$ were not explicable by such a structure. When we found here that (a) "NbCl$_4$(PMe$_2$Ph)$_2$" is actually dinuclear[4] and that (b) TaCl$_4$(PMe$_2$Ph)$_2$ is cis,[5] it was clear that a good deal more remained to be learned about this class of compounds. This paper is the first of several in which we hope to sort out some of the basic questions in this area.

Experimental Section

All manipulations were carried out under an atmosphere of argon. Standard vacuum-line techniques were used. NbCl$_5$ and the phosphine ligands were purchased from Aldrich and Strem Chemicals, Inc.,

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