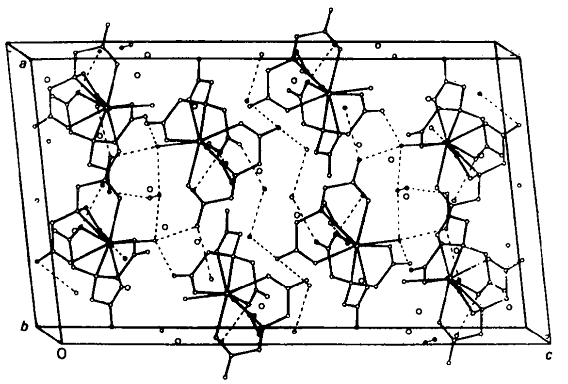

Fig. 2. View of the crystal structure. The dotted lines represent the hydrogen bonds.

four crystallographically independent potassium cations in the structure. K1, K2 and K3 ions are six coordinate (four carboxyl oxygens and two waters), the disordered K4 is five coordinate (two carboxyl oxygens and three waters). The whole structure is held together by a network of hydrogen bonds and K—O electrostatic interactions. The crystal packing is shown in Fig. 2.

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References

Bukietyńska, K. & Mondry, A. (1985). *Rare Earth Spectroscopy.* Proc. Int. Symp. Rare-Earth Spectroscopy, Wrocław, Poland, September 10–15 1984, pp. 167–173. Singapore: World Scientific.

Bukietyńska, K. & Mondry, A. (1987). *Inorg. Chim. Acta.* In the press.

Đào, C. N. (1987). PhD Dissertation. Univ. of Wrocław.

Drew, M. G. B. (1977). *Coord. Chem. Rev.* **24**, 179–275.

Fuller, C. C., Molzahn, D. K. & Jacobson, R. A. (1978). *Inorg. Chem.* **17**, 2138–2143.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Johnson, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Martin, L. L. & Jacobson, R. A. (1972*a*). *Inorg. Chem.* **11**, 2785–2789.

Martin, L. L. & Jacobson, R. A. (1972*b*). *Inorg. Chem.* **11**, 2789–2795.

Nesterova, Ya. M., Porai-Koshits, M. A., Mitrofanova, N. D. & Filippova, E. D. (1980). *Zh. Neorg. Khim.* **25**, 1999–2001.

Sinha, S. P. (1976). *Struct. Bonding (Berlin)*, **25**, 69–154.

Syntex (1976). *XTL/XTLE Structure Determination System.* Syntex Analytical Instruments, Cupertino, California, USA.

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Structures of Tetrakis(1,2-dimethylimidazole)$M^{\rm II}$ Diperchlorates ($M^{\rm II}$ = Co, $Zn_{0.98}Co_{0.02}$)

By Ernest Bernarducci, Parimal K. Bharadwaj, Joseph A. Potenza and Harvey J. Schugar

Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903, *USA*

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Abstract. $[Co(C_5H_8N_2)_4](ClO_4)_2$, $M_r = 642\cdot37$, trigonal, $P3_221$, $a = 12\cdot140\,(1)$, $c = 17\cdot399\,(2)$ Å, $V = 2220\cdot5\,(6)$ Å^3, $Z = 3$, $D_m = 1\cdot43\,(1)$, $D_x = 1\cdot442$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0\cdot71073$ Å) = $0\cdot81$ mm^{-1}, $F(000) = 999$, $T = 297\,(1)$ K, $R(F) = 0\cdot054$ for 1967 reflections. $[Co_{0.02}Zn_{0.98}(C_5H_8N_2)_4]$-$(ClO_4)_2$, $M_r = 648\cdot68$, trigonal, $P3_121$, $a = 12\cdot142\,(2)$, $c = 17\cdot420\,(1)$ Å, $V = 2224\cdot3\,(8)$ Å^3, $Z = 3$, $D_m = 1\cdot46\,(1)$, $D_x = 1\cdot453$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0\cdot71073$ Å) = $1\cdot08$ mm^{-1}, $F(000) = 1008$, $T = 298\,(1)$ K, $R(F) = 0\cdot054$ for 1590 reflections. The structures are isomorphous and contain discrete pseudotetrahedral tetrakis(1,2-dimethylimidazole)$M^{\rm II}$ cations (site symmetry 2) separated by perchlorate anions. Corresponding Co—N [1·988 (3), 2·002 (3) Å] and Zn—N [1·983 (5), 2·015 (5) Å] distances are equal to each other and closely resemble those in other pseudotetrahedral Co$^{\rm II}$ and Zn$^{\rm II}$ complexes containing imidazole or substituted imidazole ligands.

Introduction. We have been interested in metal–imidazole complexes both intrinsically and as part of a long-range project involving structural and spectroscopic studies of compounds designed to model the active sites of copper-containing proteins, many of which are either known or thought to contain Cu$^{\rm II}$–imidazole bonding (Bernarducci, Bharadwaj, Krogh-Jespersen, Potenza & Schugar, 1983). Characterization of the active sites in these proteins is facilitated by spectroscopic studies in which Cu$^{\rm II}$ is substituted by

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other divalent metal ions, M^{II}, such as Co^{II} and Ni^{II} (Hauenstein & McMillan, 1981). While recent spectroscopic studies of model imidazole and substituted imidazole complexes have helped to establish the general features of imidazole → M^{II} LMCT absorptions (Schugar, 1983), several important questions still remain. These include the effects of coordination geometry/ligand orientation on band position and intensity, and the detailed spectroscopic consequences of imidazole–imidazole interactions. Prompted by the report that Co(1,2-dimethylimidazole)$_4$ dinitrate seemed to contain a tetrahedral chromophore (Goodgame, Goodgame & Rayner Canham, 1971), and because we were unaware of any published crystallographic study of a tetrakisimidazole Co^{II} chromophore, we chose to characterize the analogous spectroscopically innocent perchlorate salt both structurally and spectroscopically. Preliminary spectroscopic results for this system have been reported (Schugar, 1983). We report here the structure of this complex as well as that of the isostructural Zn^{II} analogue which serves as a useful host lattice for the Co^{II} spectroscopic studies.

Experimental. Preparation of the tetrakis(1,2-dimethylimidazole)M^{II} diperchlorates, M = Co(1), $Zn_{0.98}Co_{0.02}$ (2): To a solution of 0·475 g (1·30 mmol) of $Co(ClO_4)_2.6H_2O$ in 20 ml acetone, a solution containing 0·500 g (5·20 mmol) of freshly distilled 1,2-dimethylimidazole in 20 ml acetone and 5 ml of 2,2′-dimethoxypropane (DMP) was added. The resulting crystals of (1) were collected and recrystallized from warm methanol. To prepare (2), 0·056 g (0·58 mmol) of 1,2-dimethylimidazole was dissolved in a solution containing 15 ml of acetone and 25 ml of DMP. In a second acetone (15 ml)/DMP (25 ml) solution, 0·052 g (0·14 mmol) of $Zn(ClO_4)_2.6H_2O$ and 0·00106 g (0·003 mmol, 2%) of $Co(ClO_4)_2.6H_2O$ were dissolved. The ligand and metal solutions were combined and pale blue crystals, nominally doped at the 2% level, precipitated almost immediately. These were collected and recrystallized from warm acetone. Caution! These compounds may explode if heated when dry.

Structure solution [values for complex (2) are given in parentheses]: D_m by flotation; blue–purple prism 0·35 × 0·35 × 0·23 mm for (1); pale blue prism 0·25 × 0·32 × 0·30 mm for (2); Enraf–Nonius CAD-4 diffractometer; graphite-monochromated Mo $K\alpha$ radiation; θ–2θ scan. Reciprocal-lattice symmetry and systematic absence ($000l$, $l = 3n$) consistent with trigonal space groups $P3_121$ ($P3_221$) and $P3_112$ ($P3_212$); $P3_221$ ($P3_121$) confirmed by successful solution of structure. Cell constants from setting angles of 25 reflections with $13·55 \le \theta \le 20·61°$ (1) and $13·52 \le \theta \le 20·60°$ (2); data corrected for Lorentz, polarization and absorption [empirical correction, ψ scan, six reflections with $\chi > 80°$; $0·96 < T < 1·00$ ($0·95 < T < 1·00$)] effects. Variation in intensity of three standard reflections <0·8%; 2592 (2599) unique reflections measured with $4 \le 2\theta \le 50°$; 1967 (1590) with $I \ge 3\sigma(I)$ used in refinement. Data collected: h, $\pm k$, $\pm l$ with $h > k$ for $k < 0$. Structures solved by direct methods (*MULTAN*82: Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and difference Fourier techniques; H atoms from difference Fouriers and at calculated positions; C—H distance = 0·95 Å; B_H set to $B_N + 1$ before final refinement cycles; H atoms not refined. Full-matrix least-squares refinement on F; all non-H atoms anisotropic; $w = 4F_o^2/[\sigma^2(F_o^2) + 0·0016F_o^4]$. To determine the absolute configuration, η values (Rogers, 1981) were refined for the S and I structures, respectively, in the enantiomorphic space groups $P3_121$ and $P3_221$. For the crystals used to collect data, this gave S in $P3_221$ for (1) and the inverse structure I in $P3_121$ for (2). However, from their method of preparation, both complexes are expected to be racemates with half of the crystals in each enantiomorphic space group. Final $R(F) = 0·054$ (0·054), $wR = 0·069$ (0·066), $S = 2·12$ (1·87), $(\Delta/\sigma)_{max} < 0·02$, $\Delta\rho_{max} = 1·05$ (0·91) e Å^{-3}; highest residuals near ClO_4 atoms with large thermal parameters; largest residuals not associated with ClO_4 groups = 0·39 (0·47) e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974); for (2), because of the low level of doping, only the Zn scattering factor was used for the metal site which was assumed to be completely occupied. Programs from Enraf–Nonius (1983) *SDP*.

Discussion. Final positional parameters and their e.s.d.'s are given in Table 1.* A view of the zinc-containing complex (2), showing the atom-numbering scheme, is given in Fig. 1, while selected bond distances and angles are listed in Table 2. The structures are isomorphous and each contains discrete tetrakis(1,2-dimethylimidazole)M^{II} cations with site symmetry 2 separated by perchlorate anions. All $M^{II}\cdots O(ClO_4)$ distances are greater than 4 Å, demonstrating the lack of direct metal–perchlorate bonding. The shortest interionic contact in each structure is N(2)···O(1) [2·997 (6) (1), 3·000 (7) Å (2)] and is presumably non-bonding: hydrogen bonding from the amine N to the perchlorate groups, as found in Zn(imidazole)$_4$.2ClO_4 (Bear, Duggan & Freeman, 1975) is precluded in the present structures by methylation at N(2).

In the cations, each M^{II} ion is situated on a twofold axis and is coordinated in a distorted tetrahedral fashion by the imine N atoms of four 1,2-dimethylimidazole groups. The N—M—N angles are similar in

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43919 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* [*values for* (2) *are listed below those for* (1)]

	x	y	z	B_{eq}(Å^2)
Co	0·21615 (8)	0	1/6	4·17 (2)
Zn	0·7824 (1)	1	5/6	4·27 (3)
Cl	−0·5040 (1)	−0·3088 (2)	0·17587 (8)	6·47 (4)
	1·5036 (2)	1·3084 (2)	0·8242 (1)	6·66 (6)
N(1)	0·2482 (4)	−0·1073 (4)	0·2393 (3)	4·5 (1)
	0·7511 (5)	1·1074 (5)	0·7609 (3)	4·2 (2)
N(2)	0·3332 (3)	−0·1681 (4)	0·3303 (2)	4·4 (1)
	0·6663 (4)	1·1671 (5)	0·6703 (3)	4·4 (1)
N(3)	0·0656 (4)	−0·1201 (4)	0·1035 (2)	4·4 (1)
	0·9341 (5)	1·1197 (5)	0·8970 (3)	4·2 (2)
N(4)	−0·1203 (4)	−0·2785 (4)	0·0706 (3)	5·0 (1)
	1·1197 (5)	1·2779 (5)	0·9300 (4)	5·2 (2)
C(1)	0·2089 (6)	−0·2668 (5)	0·3198 (4)	5·9 (2)
	0·7913 (7)	1·2657 (6)	0·6812 (5)	5·9 (2)
C(2)	0·1589 (5)	−0·2266 (6)	0·2641 (4)	5·5 (2)
	0·8412 (7)	1·2254 (7)	0·7363 (5)	5·6 (2)
C(3)	0·3546 (5)	−0·0737 (4)	0·2803 (3)	4·1 (1)
	0·6458 (6)	1·0744 (5)	0·7201 (4)	3·9 (2)
C(4)	0·0723 (5)	−0·1553 (5)	0·0290 (3)	5·0 (1)
	0·9243 (7)	1·1525 (7)	0·9715 (4)	5·2 (2)
C(5)	0·0422 (6)	0·2537 (6)	0·0090 (3)	5·7 (2)
	1·0402 (7)	1·2510 (7)	0·9899 (4)	5·7 (2)
C(6)	−0·0526 (5)	−0·1954 (5)	0·1270 (3)	4·6 (1)
	1·0516 (6)	1·1948 (6)	0·8731 (4)	4·6 (2)
C(7)	0·4758 (5)	0·0429 (5)	0·2709 (4)	5·8 (2)
	0·5245 (7)	0·9575 (7)	0·7273 (5)	6·5 (3)
C(8)	0·4272 (5)	−0·1667 (5)	0·3828 (4)	6·5 (2)
	0·5708 (7)	1·1681 (7)	0·6181 (5)	6·2 (2)
C(9)	−0·2529 (6)	−0·3863 (7)	0·0793 (5)	7·9 (2)
	1·2505 (8)	1·3846 (9)	0·9201 (6)	7·7 (3)
C(10)	−0·1058 (6)	−0·1884 (7)	0·2028 (4)	7·5 (2)
	1·1063 (7)	1·186 (1)	0·7975 (5)	7·7 (3)
O(1)	−0·6026 (5)	−0·2954 (6)	0·2046 (4)	12·7 (2)
	1·6015 (6)	1·2964 (7)	0·7945 (4)	12·2 (2)
O(2)	−0·4831 (7)	−0·2812 (7)	0·1018 (4)	13·5 (2)
	1·4797 (8)	1·2777 (8)	0·8967 (4)	13·8 (3)
O(3)	−0·4128 (5)	−0·3001 (9)	0·2212 (4)	16·1 (3)
	1·4123 (7)	1·300 (1)	0·7789 (5)	16·7 (4)
O(4)	−0·556 (1)	−0·4426 (9)	0·1561 (7)	20·0 (4)
	1·550 (1)	1·439 (1)	0·8426 (8)	20·7 (5)

$$B_{eq} = \tfrac{4}{3}\sum_i \sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

both structures; they are all within 8° of the tetrahedral angle and range from 106·2 (1) to 117·3 (3)°. This range is somewhat greater than that [108·3 (3), 113·3 (3)°] reported for the analogous but unmethylated Zn^{II}(imidazole)$_4$ diperchlorate. In (1), the Co—N bond distances are equal to those reported for the distorted tetrahedral Co(imidazole)$_2$Cl$_2$ complex [1·989 (14), 1·997 (14) Å (Antti & Lundberg, 1972)] and only slightly shorter than those found for several pseudotetrahedral CoL_2X_2 complexes where L represents an imidazole, substituted imidazole or benzimidazole ligand and X = Cl, $CH_3CO_2^-$ or $C_2H_5CO_2^-$ [2·015 (2), 2·016 (2); 2·014 (2), 2·031 (2) Å (Sundberg, Yilmaz & Mente, 1977); 2·013 (1), 2·014 (1); 2·023 (2), 2·037 (2); 2·039 (2), 2·041 (3) Å (Horrocks, Ishley & Whittle, 1982)]. The Zn—N distances are also typical and match closely the values reported for pseudotetrahedral Zn(imidazole)$_2$Cl$_2$ [1·995 (11), 2·020 (11) Å (Lundberg, 1966)], Zn(imidazole)$_4$.2ClO$_4$ [1·997 (7), 2·001 (7) Å (Bear, Duggan & Freeman, 1975)], and several other Zn(2-RIm)$_2X_2$ and Zn(imidazole)$_2X_2$ derivatives (Horrocks *et al.*, 1982). Thus, for the various distorted tetrahedral Co^{II} and Zn^{II} imidazole derivatives whose structures have been reported, the M—N distances are relatively insensitive to substitution.

The 1,2-dimethylimidazole groups are planar to within ±0·01 Å. Corresponding bond distances in these groups are equal to each other within experimental error and differ only slightly (0·009–0·025 Å) from the average of those for free imidazole determined by neutron diffraction at 293, 123 and 103 K (Craven, McMullan, Bell & Freeman, 1977; McMullan, Epstein, Ruble & Craven, 1979). In both (1) and (2), the perchlorate O atoms have large thermal parameters, possibly indicating some disorder. This is also reflected in the Cl—O bond distances which range from 1·320 (5) to 1·460 (8) Å in (1) and from 1·308 (6) to 1·432 (13) Å in (2).

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Co[Zn]—N(1)	1·988 (3)	[1·983 (5)]	N(2)—C(8)	1·455 (6)	[1·478 (8)]
Co[Zn]—N(3)	2·002 (3)	[2·015 (5)]	N(3)—C(4)	1·379 (5)	[1·380 (7)]
Cl—O(1)	1·380 (5)	[1·370 (6)]	N(3)—C(6)	1·322 (5)	[1·318 (7)]
Cl—O(2)	1·323 (5)	[1·308 (6)]	N(4)—C(5)	1·362 (6)	[1·345 (8)]
Cl—O(3)	1·320 (5)	[1·324 (6)]	N(4)—C(6)	1·351 (6)	[1·361 (8)]
Cl—O(4)	1·460 (8)	[1·432 (13)]	N(4)—C(9)	1·490 (7)	[1·474 (9)]
N(1)—C(2)	1·375 (6)	[1·366 (8)]	C(1)—C(2)	1·358 (7)	[1·352 (9)]
N(1)—C(3)	1·348 (5)	[1·337 (7)]	C(3)—C(7)	1·454 (6)	[1·452 (9)]
N(2)—C(1)	1·392 (6)	[1·398 (8)]	C(4)—C(5)	1·350 (7)	[1·353 (9)]
N(2)—C(3)	1·356 (5)	[1·342 (7)]	C(6)—C(10)	1·489 (6)	[1·503 (9)]

N(1)—Co—N(1′)	116·9 (2)	[117·3 (3)]	C(5)—N(4)—C(6)	108·1 (4)	[106·8 (6)]
N(1)—Co—N(3)	106·2 (1)	[106·4 (2)]	C(5)—N(4)—C(9)	126·9 (4)	[129·1 (6)]
N(1)—Co—N(3′)	107·2 (1)	[107·1 (2)]	C(6)—N(4)—C(9)	124·7 (4)	[123·7 (6)]
N(3)—Co—N(3′)	113·5 (2)	[112·7 (3)]	N(2)—C(1)—C(2)	105·7 (4)	[106·1 (6)]
Co[Zn]—N(1)—C(2)	125·5 (3)	[125·0 (4)]	N(1)—C(2)—C(1)	110·1 (4)	[109·5 (6)]
Co[Zn]—N(1)—C(3)	127·6 (3)	[127·6 (4)]	N(1)—C(3)—N(2)	109·5 (3)	[110·1 (5)]
C(2)—N(1)—C(3)	106·5 (3)	[107·0 (5)]	N(1)—C(3)—C(7)	125·8 (4)	[126·6 (5)]
C(1)—N(2)—C(3)	108·1 (4)	[107·3 (5)]	N(2)—C(3)—C(7)	124·6 (4)	[123·3 (6)]
C(1)—N(2)—C(8)	126·7 (4)	[126·6 (6)]	N(3)—C(4)—C(5)	108·8 (4)	[106·0 (6)]
C(3)—N(2)—C(8)	125·1 (4)	[125·9 (6)]	N(4)—C(5)—C(4)	106·7 (4)	[109·5 (5)]
Co[Zn]—N(3)—C(4)	124·6 (3)	[123·1 (4)]	N(3)—C(6)—N(4)	109·7 (4)	[109·2 (5)]
Co[Zn]—N(3)—C(6)	127·8 (3)	[127·4 (4)]	N(3)—C(6)—C(10)	125·9 (4)	[126·3 (6)]
C(4)—N(3)—C(6)	106·8 (4)	[108·5 (5)]	N(4)—C(6)—C(10)	124·4 (4)	[124·4 (6)]

Numbers in parentheses are estimated standard deviations in the least significant digits. Values for the Co-doped zinc complex are given in square brackets.

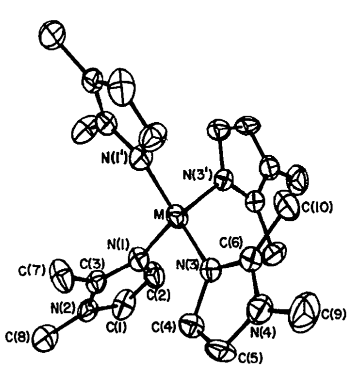

Fig. 1. View of the tetrakis(1,2-dimethylimidazole)M^{II} cation showing the atom-numbering scheme. H atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 33% probability level. The view is of a zinc-containing cation in $P3_121$.

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References

ANTTI, C.-J. & LUNDBERG, K. S. (1972). *Acta Chem. Scand.* **26**, 3995–4000.

BEAR, C. A., DUGGAN, K. A. & FREEMAN, H. C. (1975). *Acta Cryst.* B**31**, 2713–2715.

BERNARDUCCI, E., BHARADWAJ, P. K., KROGH-JESPERSEN, K., POTENZA, J. A. & SCHUGAR, H. J. (1983). *J. Am. Chem. Soc.* **105**, 3860–3866.

CRAVEN, B. M., MCMULLAN, R. K., BELL, J. D. & FREEMAN, H. C. (1977). *Acta Cryst.* B**33**, 2585–2589.

Enraf–Nonius (1983). *Structure Determination Package.* Enraf–Nonius, Delft, The Netherlands.

GOODGAME, D. M. L., GOODGAME, M. & RAYNER CANHAM, G. W. (1971). *J. Chem. Soc. A*, pp. 1923–1926.

HAUENSTEIN, B. L. & MCMILLAN, D. R. (1981). *Metal Ions in Biological Systems*, Vol. 13, edited by H. SIGEL, ch. 10. New York: Marcel Dekker.

HORROCKS, W. D. JR., ISHLEY, J. N. & WHITTLE, R. R. (1982). *Inorg. Chem.* **21**, 3265–3269, 3270–3274.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

LUNDBERG, B. K. S. (1966). *Acta Cryst.* **21**, 901–909.

MCMULLAN, R. K., EPSTEIN, J., RUBLE, J. R. & CRAVEN, B. M. (1979). *Acta Cryst.* B**35**, 688–691.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

ROGERS, D. (1981). *Acta Cryst.* A**37**, 734–741.

SCHUGAR, H. J. (1983). *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*, edited by K. D. KARLIN & J. ZUBIETA, pp. 43–74. New York: Adenine Press.

SUNDBERG, R. J., YILMAZ, I. & MENTE, D. C. (1977). *Inorg. Chem.* **16**, 1470–1476.

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[Bis(1-amino-13-methyl-3,6,9,12-tetraazapentadec-12-en-14-one oximato-*N*,*N*′,*N*′′,*N*′′′,*N*′′′′,*N*′′′′′)hydrogen(I)]dinickel(II) Triperchlorate

BY JORMA KORVENRANTA AND HEIKKI SAARINEN

Department of Inorganic Chemistry, University of Helsinki, Vuorikatu 20, 00100 *Helsinki* 10, *Finland*

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Abstract. $[Ni_2(C_{12}H_{27}N_6O)_2H](ClO_4)_3$, $M_r = 959{\cdot}56$, monoclinic, $C2/c$, $a = 25{\cdot}404\ (8)$, $b = 10{\cdot}276\ (3)$, $c = 15{\cdot}760\ (5)$ Å, $\beta = 91{\cdot}60\ (3)°$, $V = 4113\ (2)$ Å^3, $Z = 4$, $D_m = 1{\cdot}55$, $D_x = 1{\cdot}549$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 11{\cdot}9$ cm^{-1}, $F(000) = 2008$, room temperature, $R = 0{\cdot}052$ for 3129 unique reflections. The structure consists of perchlorate anions and dinuclear complex cations. The two halves of the dimer are bridged by an O···H···O hydrogen bond between the oxime O atoms [O···O, 2·428 (6) Å]. The hydrogen bond is symmetrical as a result of crystallographic requirements. The Ni^{II} is bonded to the N-donor atoms of the hexadentate ligand in a distorted octahedral coordination environment.

Introduction. In the course of our studies on octahedral Ni^{II} and Ni^{IV} complexes of oxime ligands we discovered that the Ni—N(oxime) distance as well as the geometry of the oxime group are strongly dependent on whether or not the oxime proton is preserved on coordination (Korvenranta, Saarinen & Näsäkkälä, 1982). The present compound was examined by X-ray diffraction analysis after its stoichiometry was found to correspond to the composition $Ni_2L_2H(ClO_4)_3$ (HL is a neutral oxime). This suggests that only one of the two oxime groups in the complex is deprotonated, and it was of interest to determine the structural characteristics of the oxime function in such a hybrid structure. The hexadentate amine–imine–oxime ligand used here is especially attractive as it allows stabilization of a formally trivalent nickel complex $Ni^{III}L^{2+}$ (Chakravorty, 1985).

Experimental. The ligand HL was obtained by 1:1 condensation of 2,3-butanedione monoxime and tetraethylenepentamine. The complex was prepared by reacting the ligand with nickel(II) perchlorate in aqueous ethanol. Brown, block-like crystals grown from aqueous solution by slow cooling, crystal dimensions $0{\cdot}2 \times 0{\cdot}3 \times 0{\cdot}3$ mm; D_m by flotation in $HCCl_3/CCl_4$. Nicolet *P*3 four-circle diffractometer, graphite-monochromated Mo $K\alpha$; cell parameters from 20 reflections, $9 < 2\theta < 27°$; monoclinic Cc or $C2/c$ from systematic absences, $C2/c$ confirmed by refinement; ω-scan technique, scan rate $2{\cdot}0$–$29{\cdot}3°$ min^{-1}, two standards measured every 58 reflections, no significant variations;

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