

$\text{FeCl}_3(\text{POCl}_3)$, $2\text{FeCl}_3[\text{MeSe}(\text{CH}_2)_3\text{SeMe}]$, and $\text{FeCl}_3(\text{PR}_3)$ ($R = \text{Ph}$, cyclohexyl), these varied complexes have not been previously characterized structurally (Walker & Poli, 1989*b*, and references therein). The structure of $[\text{ZnCl}(\text{C}_4\text{H}_8\text{O})(\mu\text{-Cl})]_\infty$ has been reported (Bottomley, Ferris & White, 1989).

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Structures of 2,2,2,2,2-Pentaammine-1-aqua-1,2-(μ -imidazolato-*N,N'*)-1-(iminodiacetato-*O,O'*)cobalt(III)copper(II) Perchlorate Trihydrate and 2,2,2,2,2,3,3,3,3,3-Decaammine-1,2;1,3-di-(μ -imidazolato-*N,N'*)-1-(iminodiacetato-*O,O'*)dicobalt(III)copper(II) Perchlorate Tetrahydrate

BY CHEN DONG, LIU ZHIJUN, TANG WENXIA AND DAI ANBANG

Coordination Chemistry Institute, Nanjing University, Nanjing, People's Republic of China

AND LIU WANGXI, WANG BOYI, WANG MING AND ZHENG PEIJU

Research Center of Analysis and Measurement, Fudan University, Shanghai, People's Republic of China

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Abstract. Complex (I): $[(\text{C}_4\text{H}_5\text{NO}_4)(\text{H}_2\text{O})\text{Cu}(\mu\text{-C}_3\text{H}_3\text{N}_2)\text{Co}(\text{NH}_3)_5](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$, $M_r = 676.7$, monoclinic, $P2_1/c$, $a = 13.024$ (2), $b = 15.400$ (2), $c = 13.198$ (4) Å, $\beta = 111.28$ (2)°, $V = 2466.5$ Å³, $Z = 4$, $D_x = 1.822$ g cm⁻³, $\mu(\text{Mo } K\alpha, \lambda = 0.71070 \text{ Å}) = 18.4$ cm⁻¹, $F(000) = 1388$, $T = 298$ K, $R = 0.062$ for 2859 significant reflections. Cu^{II} and Co^{III} are bridged by Im (imidazolate). Cu^{II} shows a square-pyramidal coordination by two N atoms and two O atoms of Ida (iminodiacetate) and Im in the equatorial plane, and by a water on the axis. Complex (II): $[(\text{NH}_3)_5\text{Co}(\mu\text{-C}_3\text{H}_3\text{N}_2)\text{Cu}(\text{C}_4\text{H}_5\text{NO}_4)(\mu\text{-C}_3\text{H}_3\text{N}_2)\text{Co}(\text{NH}_3)_5](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$, $M_r = 1086.8$, monoclinic, $P2_1/n$, $a = 15.617$ (2), $b = 8.876$ (1), $c = 28.801$ (4) Å, $\beta = 105.42$ (1)°, $V = 3848.8$ Å³, $Z = 4$, $D_x = 1.876$ g cm⁻³, $\mu(\text{Mo } K\alpha, \lambda = 0.71070 \text{ Å}) = 17.66$ cm⁻¹, $F(000) = 2228$, $T = 298$ K, $R = 0.073$ for 2440 significant reflections. Two Im anions connect two Co^{III} atoms to one Cu^{II} atom forming a heterotrimeric complex. The Cu^{II} also shows a square-pyramidal coordination by three N atoms and one O atom of Ida and Im in the equatorial plane and another O atom of Ida on the axis. The plane of Ida is somewhat distorted.

Introduction. At the active site of superoxide dismutase (SOD) Cu^{II} and Zn^{II} are bridged by an imidazolato (Im) anion (deprotonated imidazole) and the Cu^{II} atom shows a distorted square-pyramidal coordination, being bonded to four N atoms and one O atom (Tainer, Getzoff, Beem, Richardson & Richardson, 1982). In order to find out the relationship between the activity and the configuration of SOD, a series of Im-bridged heteronuclear complexes have been synthesized and crystallized. As part of our research programme, we now report the crystal structures of the two title Im-bridged heteronuclear complexes.

Experimental. Complex (I): small green block crystals from a water solution. Accurate cell dimensions were determined on a CAD-4 diffractometer by least-squares treatment of the setting angles of 25 reflections in the range $14.4 < \theta < 16.8^\circ$. Crystal dimensions $0.15 \times 0.15 \times 0.15$ mm; intensities of reflections with indices $h - 15$ to 15, $k 0$ to 18, $l 0$ to 15, with $0 < 2\theta < 50^\circ$ were measured; ω - 2θ scans; ω -scan width $(0.80 + 0.35 \tan \theta)^\circ$, graphite-monochromated Mo $K\alpha$ radiation. Intensities of three

Table 1. Atomic parameters (with their estimated standard deviations) of non-H atoms of complex (I)

$$B_{\text{eq}} = \frac{4}{3}(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + abc\cos\gamma\beta_{12} + accos\beta\beta_{13} + bccos\alpha\beta_{23}).$$

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
Cu	0.48532 (9)	0.16135 (7)	-0.31474 (8)	2.61 (2)
Co	0.77391 (9)	0.06846 (8)	0.13154 (9)	2.09 (2)
Cl(1)	0.1872 (2)	0.2551 (2)	-0.3140 (2)	4.65 (7)
Cl(2)	0.9068 (2)	0.1094 (2)	0.8180 (2)	5.54 (8)
O(1)	0.2664 (6)	-0.0278 (5)	-0.4074 (5)	4.3 (2)
O(2)	0.4143 (5)	0.0487 (4)	-0.3145 (5)	3.2 (1)
O(3)	0.5108 (5)	0.2827 (4)	-0.3427 (5)	3.0 (1)
O(4)	0.4266 (5)	0.3921 (4)	-0.4496 (5)	3.5 (2)
O(5)	0.132 (2)	0.279 (2)	-0.426 (2)	8.9 (6)*
DO(5)†	0.089 (2)	0.226 (2)	-0.391 (2)	9.9 (7)*
O(6)	0.167 (1)	0.3086 (8)	-0.2379 (9)	9.3 (3)*
O(7)	0.302 (1)	0.264 (1)	-0.299 (1)	8.9 (5)*
DO(7)†	0.243 (3)	0.324 (3)	-0.354 (3)	11 (1)*
O(8)	0.185 (3)	0.167 (2)	-0.280 (3)	13 (1)*
DO(8)†	0.262 (2)	0.186 (2)	-0.278 (2)	8.3 (6)*
O(9)	0.846 (1)	0.1598 (9)	0.724 (1)	10.5 (4)*
O(10)	0.858 (1)	0.138 (1)	0.885 (1)	15.7 (6)*
O(11)	1.017 (1)	0.1395 (8)	0.8448 (9)	9.5 (3)*
O(12)	0.905 (2)	0.023 (1)	0.780 (1)	10.0 (5)*
DO(12)†	0.933 (3)	0.042 (3)	0.893 (3)	11 (1)*
O(13)	0.0024 (8)	0.6601 (7)	0.1203 (8)	7.5 (3)*
O(14)	0.4117 (8)	0.4198 (7)	0.8103 (8)	6.9 (2)*
O(15)	0.3808 (6)	0.5853 (6)	0.8703 (7)	5.4 (2)
O(16)	0.061 (2)	0.577 (1)	0.959 (2)	9.8 (5)*
DO(16)†	0.097 (3)	0.642 (2)	0.963 (3)	11 (1)*
N(1)	0.3943 (6)	0.1591 (5)	-0.4737 (5)	2.7 (2)
N(2)	0.5706 (6)	0.1711 (5)	-0.1592 (5)	2.7 (2)
N(3)	0.6845 (6)	0.1354 (5)	0.0074 (5)	2.4 (2)
N(4)	0.7987 (6)	-0.0190 (5)	0.0306 (6)	3.1 (2)
N(5)	0.6415 (6)	0.0074 (5)	0.1298 (5)	2.5 (2)
N(6)	0.8668 (7)	-0.0003 (6)	0.2590 (6)	3.6 (2)
N(7)	0.7470 (6)	0.1517 (5)	0.2332 (5)	2.7 (2)
N(8)	0.9079 (6)	0.1316 (6)	0.1338 (6)	3.7 (2)
C(1)	0.3289 (8)	0.0344 (6)	-0.3994 (7)	3.1 (2)
C(2)	0.2997 (8)	0.0993 (6)	-0.4927 (7)	3.1 (2)
C(3)	0.3641 (8)	0.2499 (6)	-0.5112 (7)	3.0 (2)
C(4)	0.4394 (7)	0.3131 (6)	-0.4287 (7)	2.6 (2)
C(5)	0.6161 (7)	0.1055 (6)	-0.0901 (6)	2.3 (2)
C(6)	0.6106 (8)	0.2465 (6)	-0.1040 (7)	3.2 (2)
C(7)	0.6806 (8)	0.2254 (6)	-0.0013 (7)	3.2 (2)

* Isotropic thermal parameters.

† Some O atoms of the ClO_4^- anions are disordered. The atoms labelled 'DO' are the disordered counterparts of the O atoms.

reflections measured every 1 h showed no evidence of crystal decay. 4546 reflections collected, 4340 unique, 2859 with $I > 3\sigma(I)$ labelled observed and used in structure solution and refinement. Corrected for Lorentz, polarization and absorption effects (max. and min. transmission factors 1.000 and 0.850), Gaussian integration, grid $8 \times 8 \times 8$. The coordinates of the Cu and Co atoms were determined by direct methods. The coordinates of the remaining non-H atoms were found by subsequent difference Fourier syntheses. No attempts were made to locate H atoms. Some atoms of ClO_4^- groups were disordered, the occupancy of the disordered atoms was fixed to 0.5. Refinement by full-matrix least-squares calculations on F , initially with isotropic and then with anisotropic thermal parameters, disordered O atoms were refined with isotropic thermal parameters. The final cycle of refinement included 281 variable parameters. $R = 0.062$, $wR = 0.072$, $w = 1$ when $F^2 > 3\sigma(F^2)$. Max. shift/e.s.d. = 0.04, $S = 3.56$, density in final difference map $\pm 0.78 \text{ e \AA}^{-3}$. Scattering factors and anomalous-dispersion corrections were from

Table 2. Atomic parameters (with their estimated standard deviations) of non-H atoms of complex (II)

$$B_{\text{eq}} = \frac{4}{3}(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + abc\cos\gamma\beta_{12} + accos\beta\beta_{13} + bccos\alpha\beta_{23}).$$

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
Cu	0.9821 (2)	0.2946 (4)	0.3706 (1)	1.82 (7)
Co(1)	1.2233 (2)	-0.1539 (4)	0.4899 (1)	2.35 (9)
Co(2)	1.0400 (2)	-0.0167 (4)	0.2022 (1)	1.59 (7)
Cl(1)	1.1500 (4)	0.5494 (8)	0.3096 (2)	2.8 (2)
Cl(2)	0.9649 (5)	0.2267 (9)	0.0478 (3)	3.6 (2)
Cl(3)	0.3507 (4)	0.0641 (8)	0.6866 (2)	2.7 (2)
Cl(4)	1.3103 (5)	0.0764 (8)	0.3521 (2)	3.2 (2)
O(1)	1.004 (1)	0.481 (2)	0.4095 (6)	2.7 (4)*
O(2)	0.8538 (9)	0.256 (2)	0.3937 (5)	1.9 (3)*
O(3)	0.713 (1)	0.319 (2)	0.3698 (6)	3.3 (4)*
O(4)	0.990 (1)	0.728 (3)	0.4036 (7)	4.9 (5)*
O(5)	1.238 (2)	0.589 (3)	0.317 (1)	9.5 (8)*
O(6)	1.124 (2)	0.464 (4)	0.270 (1)	9.9 (8)*
O(7)	1.141 (2)	0.455 (3)	0.3486 (9)	8.7 (8)*
O(8)	1.098 (1)	0.685 (2)	0.3090 (7)	4.6 (5)*
O(9)	1.046 (1)	0.233 (3)	0.0843 (7)	5.3 (5)*
O(10)	0.927 (2)	0.374 (4)	0.048 (1)	12 (1)*
O(11)	0.976 (2)	0.214 (4)	0.003 (1)	9.2 (8)*
O(12)	0.910 (2)	0.121 (4)	0.058 (1)	10.3 (9)*
O(13)	0.388 (2)	0.182 (3)	0.7176 (9)	7.2 (6)*
O(14)	0.410 (1)	0.039 (3)	0.6587 (8)	5.9 (6)*
O(15)	0.341 (1)	-0.064 (2)	0.7150 (7)	4.8 (5)*
O(16)	0.272 (2)	0.109 (3)	0.6575 (9)	7.7 (7)*
O(17)	1.392 (2)	0.030 (3)	0.3430 (9)	8.1 (7)*
O(18)	1.334 (2)	0.147 (3)	0.3968 (8)	6.9 (6)*
O(19)	1.258 (2)	-0.051 (3)	0.3529 (9)	7.5 (7)*
O(20)	1.267 (1)	0.174 (3)	0.3145 (8)	6.2 (6)*
O(21)	1.324 (1)	0.479 (3)	0.4415 (7)	5.8 (6)*
O(22)	0.959 (1)	0.689 (3)	0.0840 (7)	5.4 (5)*
O(23)	0.096 (3)	0.100 (5)	0.553 (1)	16 (1)*
O(24)	0.922 (2)	0.528 (4)	0.490 (1)	13 (1)*
N(1)	0.973 (1)	0.134 (2)	0.3226 (7)	1.7 (4)*
N(2)	0.997 (1)	0.021 (2)	0.2587 (6)	1.4 (4)*
N(3)	1.083 (1)	0.202 (2)	0.4176 (7)	2.1 (4)*
N(4)	1.175 (1)	0.031 (2)	0.4607 (7)	2.2 (4)*
N(5)	0.922 (1)	0.048 (2)	0.1605 (7)	2.0 (4)*
N(6)	1.079 (1)	0.199 (3)	0.2024 (7)	2.9 (5)*
N(7)	1.081 (1)	-0.056 (2)	0.1441 (7)	1.9 (4)*
N(8)	1.157 (1)	-0.078 (2)	0.2437 (7)	2.2 (4)*
N(9)	1.001 (1)	-0.234 (2)	0.2025 (7)	2.3 (5)*
N(10)	1.261 (1)	-0.056 (2)	-0.5537 (7)	2.4 (5)*
N(11)	1.111 (2)	-0.201 (3)	0.5039 (9)	4.7 (6)*
N(12)	1.338 (1)	-0.104 (3)	0.4770 (8)	3.6 (5)*
N(13)	1.188 (1)	-0.248 (2)	0.4259 (7)	2.6 (5)*
N(14)	1.271 (2)	-0.353 (4)	0.520 (1)	6.9 (8)*
N(15)	0.892 (1)	0.432 (2)	0.3227 (6)	1.8 (4)*
C(1)	0.908 (1)	0.030 (3)	0.3066 (8)	1.7 (5)*
C(2)	0.919 (2)	-0.041 (3)	0.2668 (8)	2.1 (5)*
C(3)	1.029 (2)	0.122 (3)	0.2935 (9)	2.0 (5)*
C(4)	1.098 (2)	0.053 (3)	0.4264 (9)	2.3 (6)*
C(5)	1.209 (2)	0.174 (4)	0.476 (1)	5.5 (9)*
C(6)	1.149 (2)	0.282 (4)	0.449 (1)	4.5 (7)*
C(7)	0.970 (2)	0.596 (3)	0.3859 (9)	2.2 (6)*
C(8)	0.910 (1)	0.590 (3)	0.3369 (8)	1.9 (5)*
C(9)	0.799 (1)	0.381 (3)	0.3161 (8)	1.9 (5)*
C(10)	0.790 (2)	0.316 (3)	0.3634 (9)	2.2 (6)*

* Isotropic thermal parameters.

International Tables for X-ray Crystallography (1974). All calculations were performed on a PDP 11/44 computer using the *SDP* package (Enraf-Nonius, 1983). Atomic coordinates are given in Table 1, bond distances and angles in Table 3.* Fig. 1 shows the structure of the $[(\text{Ida})\text{CuImCo}(\text{NH}_3)_5]^{2+}$ cation (Ida = iminodiacetate).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52763 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Bond distances (Å) and bond angles (°)

Complex (I)			
Cu—N(1)	2.001 (4)	O(2)—C(1)	1.279 (6)
Cu—N(2)	1.953 (4)	O(3)—C(4)	1.268 (5)
Co—N(3)	1.928 (4)	O(4)—C(4)	1.246 (6)
Co—N(4)	2.001 (4)	N(1)—C(2)	1.484 (6)
Co—N(5)	1.957 (4)	N(1)—C(3)	1.488 (6)
Co—N(6)	1.984 (4)	N(2)—C(5)	1.346 (6)
Co—N(7)	1.977 (4)	N(2)—C(6)	1.369 (7)
Co—N(8)	1.989 (4)	N(3)—C(5)	1.353 (6)
Cu—O(2)	1.966 (3)	N(3)—C(7)	1.389 (6)
Cu—O(3)	1.956 (3)	C(1)—C(2)	1.524 (7)
Cu—O(15)	2.425 (4)	C(3)—C(4)	1.523 (7)
O(1)—C(1)	1.236 (6)	C(6)—C(7)	1.369 (7)
O(2)—Cu—O(3)	162.8 (2)	N(7)—Co—N(8)	92.5 (2)
O(2)—Cu—O(15)	87.9 (2)	Cu—O(2)—C(1)	114.3 (3)
O(2)—Cu—N(1)	83.5 (2)	Cu—O(3)—C(4)	113.7 (3)
O(2)—Cu—N(2)	98.9 (2)	Cu—N(1)—C(2)	109.1 (3)
O(3)—Cu—O(15)	102.4 (2)	Cu—N(1)—C(3)	108.5 (3)
O(3)—Cu—N(1)	84.0 (2)	C(2)—N(1)—C(3)	115.1 (4)
O(3)—Cu—N(2)	93.1 (2)	Cu—N(2)—C(5)	126.7 (4)
O(15)—Cu—N(1)	83.8 (2)	Cu—N(2)—C(6)	125.9 (3)
O(15)—Cu—N(2)	99.1 (2)	C(5)—N(2)—C(6)	106.6 (4)
N(1)—Cu—N(2)	176.3 (2)	Co—N(3)—C(5)	127.7 (3)
N(3)—Co—N(4)	89.3 (2)	Co—N(3)—C(7)	126.6 (3)
N(3)—Co—N(5)	89.4 (2)	C(5)—N(3)—C(7)	105.6 (4)
N(3)—Co—N(6)	179.6 (2)	O(1)—C(1)—O(2)	123.0 (5)
N(3)—Co—N(7)	91.6 (2)	O(1)—C(1)—C(2)	118.4 (5)
N(3)—Co—N(8)	90.4 (2)	O(2)—C(1)—C(2)	118.5 (5)
N(4)—Co—N(5)	91.3 (2)	N(1)—C(2)—C(1)	108.8 (4)
N(4)—Co—N(6)	90.5 (2)	N(1)—C(3)—C(4)	109.8 (4)
N(4)—Co—N(7)	178.0 (2)	O(3)—C(4)—O(4)	123.7 (5)
N(4)—Co—N(8)	89.2 (2)	O(3)—C(4)—C(3)	118.5 (4)
N(5)—Co—N(6)	91.0 (2)	O(4)—C(4)—C(3)	117.8 (4)
N(5)—Co—N(7)	87.0 (2)	N(2)—C(5)—N(3)	111.4 (4)
N(5)—Co—N(8)	179.4 (2)	N(2)—C(6)—C(7)	108.3 (5)
N(6)—Co—N(7)	88.5 (2)	N(3)—C(7)—C(6)	108.1 (5)
N(6)—Co—N(8)	89.2 (2)		
Complex (II)			
Cu—O(1)	1.975 (6)	N(1)—C(3)	1.364 (10)
Cu—O(2)	2.301 (5)	N(2)—C(2)	1.413 (10)
Cu—N(1)	1.966 (7)	N(2)—C(3)	1.337 (10)
Cu—N(3)	1.960 (7)	N(3)—C(4)	1.357 (11)
Cu—N(15)	2.078 (7)	O(1)—C(7)	1.268 (10)
Co(1)—N(4)	1.907 (7)	O(2)—C(10)	1.259 (9)
Co(1)—N(10)	1.978 (7)	O(3)—C(10)	1.264 (9)
Co(1)—N(11)	1.957 (8)	O(4)—C(7)	1.282 (10)
Co(1)—N(12)	1.984 (8)	N(3)—C(6)	1.367 (11)
Co(1)—N(13)	1.965 (7)	N(4)—C(4)	1.351 (10)
Co(1)—N(14)	2.015 (11)	N(4)—C(5)	1.394 (13)
Co(2)—N(2)	1.948 (6)	N(15)—C(8)	1.469 (11)
Co(2)—N(5)	2.003 (7)	N(15)—C(9)	1.489 (10)
Co(2)—N(6)	2.004 (8)	C(1)—C(2)	1.364 (11)
Co(2)—N(7)	1.977 (7)	C(5)—C(6)	1.426 (14)
Co(2)—N(8)	1.975 (7)	C(7)—C(8)	1.472 (11)
Co(2)—N(8)	2.025 (7)	C(9)—C(10)	1.523 (12)
N(1)—C(1)	1.364 (10)		
O(1)—Cu—O(2)	89.7 (2)	N(5)—Co(2)—N(6)	87.4 (3)
O(1)—Cu—N(1)	167.0 (3)	N(5)—Co(2)—N(7)	89.9 (3)
O(1)—Cu—N(3)	88.3 (3)	N(5)—Co(2)—N(8)	179.1 (3)
O(1)—Cu—N(15)	82.7 (3)	N(5)—Co(2)—N(9)	92.5 (3)
O(2)—Cu—N(1)	101.2 (2)	N(6)—Co(2)—N(7)	90.3 (3)
O(2)—Cu—N(3)	109.9 (2)	N(6)—Co(2)—N(8)	91.8 (3)
O(2)—Cu—N(15)	78.1 (2)	N(6)—Co(2)—N(9)	179.5 (3)
N(1)—Cu—N(3)	94.3 (3)	N(7)—Co(2)—N(8)	90.5 (3)
N(1)—Cu—N(15)	92.8 (3)	N(7)—Co(2)—N(9)	90.1 (3)
N(3)—Cu—N(15)	168.0 (3)	N(8)—Co(2)—N(9)	88.3 (3)
N(4)—Co(1)—N(10)	91.0 (3)	C(1)—N(1)—C(3)	106.4 (7)
N(4)—Co(1)—N(11)	90.2 (3)	C(2)—N(2)—C(3)	107.7 (7)
N(4)—Co(1)—N(12)	89.7 (3)	C(4)—N(3)—C(6)	108.4 (8)
N(4)—Co(1)—N(13)	98.4 (3)	C(4)—N(4)—C(5)	106.7 (8)
N(4)—Co(1)—N(14)	178.3 (3)	C(8)—N(15)—C(9)	115.4 (7)
N(10)—Co(1)—N(11)	87.9 (3)	N(1)—C(1)—C(2)	110.1 (7)
N(10)—Co(1)—N(12)	90.9 (3)	N(2)—C(2)—C(1)	105.5 (7)
N(10)—Co(1)—N(13)	178.6 (3)	N(1)—C(3)—N(2)	110.1 (7)
N(10)—Co(1)—N(14)	90.2 (4)	N(3)—C(4)—N(4)	110.9 (8)
N(11)—Co(1)—N(12)	178.8 (4)	N(4)—C(5)—C(6)	107.4 (9)
N(11)—Co(1)—N(13)	93.3 (3)	N(3)—C(6)—C(5)	107.1 (1)
N(11)—Co(1)—N(14)	88.6 (4)	O(1)—C(7)—O(4)	120.3 (8)
N(12)—Co(1)—N(13)	87.9 (3)	O(1)—C(7)—C(8)	123.5 (8)
N(12)—Co(1)—N(14)	91.5 (4)	O(4)—C(7)—C(8)	116.1 (9)
N(13)—Co(1)—N(14)	90.4 (4)	N(15)—C(8)—C(7)	109.2 (7)
N(2)—Co(2)—N(5)	89.1 (3)	N(15)—C(9)—C(10)	109.0 (7)
N(2)—Co(2)—N(6)	90.2 (3)	O(2)—C(10)—O(3)	121.4 (8)
N(2)—Co(2)—N(7)	178.8 (3)	O(2)—C(10)—C(9)	122.1 (7)
N(2)—Co(2)—N(8)	90.6 (3)	O(3)—C(10)—C(9)	116.5 (8)
N(2)—Co(2)—N(9)	89.3 (3)		

Complex (II): brown needle crystals grown from a water solution. Data collection and refinement were as for complex (I). Unit cell by least squares on 25 reflections, $11.5 < \theta < 16.2^\circ$; crystal dimensions $0.07 \times 0.14 \times 0.21$ mm; intensities of reflections with indices $h - 16$ to 16 , $k 0$ to 9 , $l 0$ to 30 , with $2 < 2\theta < 44^\circ$ were measured; ω -scan width $(0.70 + 0.35 \tan \theta)^\circ$, 5231 reflections measured, 5110 unique, 2440 with $F^2 > 3\sigma(F^2)$ used to solve the structure; max. and min. transmission factors 0.998 and 0.885. Method used to solve the structure was also the same as for complex (I), only the Cu, Co and Cl atoms were refined with anisotropic thermal parameters. The final cycle of refinement included 342 variable parameters. $R = 0.073$, $wR = 0.084$, $w = 1$ when $F^2 > 3\sigma(F^2)$. Max. shift/e.s.d. = 0.03, $S = 9.96$, density in final difference map $\pm 0.696 \text{ e } \text{Å}^{-3}$. Atomic coordinates are given in Table 2, bond distances and angles in Table 3. Fig. 2 shows the structure of the $[(\text{NH}_3)_5\text{CoImCu}(\text{Ida})\text{ImCo}(\text{NH}_3)_5]^{14+}$ cation.

Discussion. The structure of the Im-bridged hetero-binuclear complex (I) consists of an $[(\text{Ida})\text{CuIm}$

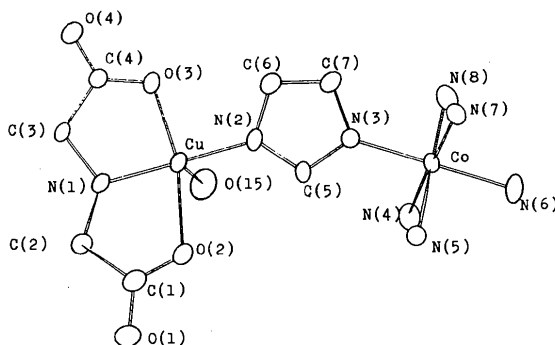


Fig. 1. Structure of the complex (I) cation.

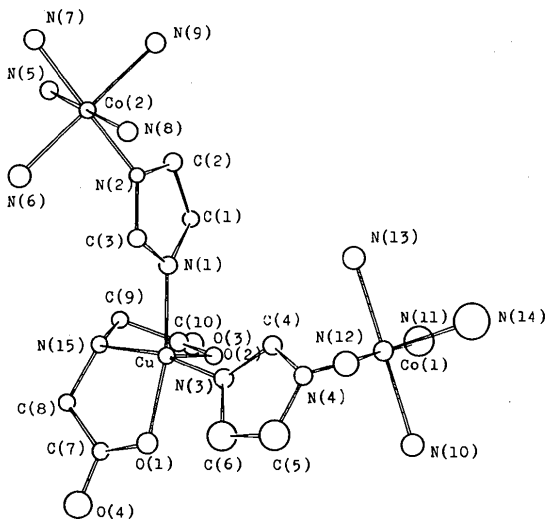


Fig. 2. Structure of the complex (II) cation.

$\text{Co}(\text{NH}_3)_5]^{2+}$ cation, two ClO_4^- anions and four H_2O 's. In this cation, the Im anion bridges the Cu and Co atoms (Fig. 1). The Cu atom shows a distorted square-pyramidal coordination, surrounded by the approximately planar O(2), O(3) and N(1) from Ida and N(2) from Im, and a water on the axis. The Cu atom is 0.13 Å above the equatorial plane. The bond length Cu—O(15) 2.43 Å is longer than Cu—N(1), Cu—N(2), Cu—O(2) and Cu—O(3) in the equatorial plane. All the Cu—N and Cu—O bond distances accord with literature values (Hathaway & Billing, 1970). The Co atom is surrounded by six N atoms, five of which are from NH_3 's and one from the Im group, forming a regular octahedral coordination. The bond distances and angles around the Co atom are in accord with similar values in the literature (Davis, Dewan & Lippard, 1981).

The coordinated Im and Ida groups show good planar conformation. The Im plane makes an angle of 22° with the square-pyramidal base plane [N(1), O(2), N(2), O(3)] and of 19.5° with the Ida-group plane. The Im plane almost divides the angles of N(4)—Co—N(5) and N(7)—Co—N(8) equally. The bond distances and the angles in the Im group are close to those in a free imidazole molecule (Sundberg & Martin, 1974). The bond distances N—C and C—C of the Ida group are similar to those in $\text{H}_2\text{Ida.HCl}$ (Oskarsson, 1973).

The structure of the Im-bridged heterotrinary complex (II) consists of $[(\text{NH}_3)_5\text{CoImCu}(\text{Ida})\text{Im-Co}(\text{NH}_3)_5]^{4+}$, four ClO_4^- anions and four H_2O 's. The Cu atom is coordinated by three N atoms and two O atoms, of which two N atoms are from two Im groups and the others from the Ida group, forming a square-pyramidal configuration as shown in Fig. 2. N(1), N(3), O(1) and N(15) form the equatorial plane and the Cu atom is located at the centre and 0.18 Å above this plane. The average bond distance

of Cu—N_{Im} 1.963 Å is shorter than Cu—N_{Ida} 2.078 Å. The bond distance of the O(2) atom of Ida coordinated to Cu at the top of the square pyramid, 2.301 Å, is longer than that of Cu—O(1), 1.975 Å, which is in the equatorial plane. The Co configuration is the same as that in complex (I).

The non-H atoms in the Im group show a good planar conformation. The angle of each of the two Im planes with the equatorial plane of Cu is 81 and 29°, and the angle of the two Im planes is 84°. The bond distances in the Im groups are similar to those in the free imidazole molecule (Sundberg & Martin, 1974).

Compared with complex (I), the conformation of the coordinated Ida has changed. When the second $[(\text{NH}_3)_5\text{CoIm}]^{2+}$ group coordinates to the Cu^{II} atom of $[(\text{Ida})\text{CuImCo}(\text{NH}_3)_5]^{2+}$, the plane of the Ida folds forming two planes. The angle between the two planes is 110.3°. One O atom of Ida coordinates with Cu in the equatorial plane while the other O atom is on the axis. The conformation of Ida may be changed by $[(\text{NH}_3)_5\text{CoIm}]^{2+}$ which has a larger steric effect than H_2O . The bond distances C—C and C—N of the Ida are the same in the two complexes.

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Structure of a Nickel(II) Complex of the Deprotonated Anion of 3,9-Dimethyl-4,8-diaza-3,8-undecadiene-2,10-dione Dioxime

BY YUN-MING WANG, CHUNG-SUN CHUNG,* CHIH-YI CHENG AND SUE-LEIN WANG

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 30043

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Abstract. Bis{3,3'-(trimethylenedinitrilo)di[2-butanone oximato(1-)]}nickel(II) perchlorate, $[\text{Ni}$

$(\text{C}_{11}\text{H}_{19}\text{N}_4\text{O}_2)](\text{ClO}_4)$, $M_r = 397.5$, monoclinic, $P2_1/c$, $a = 7.162$ (3), $b = 16.805$ (7), $c = 13.703$ (5) Å, $\beta = 102.70$ (3)°, $V = 1609$ (1) Å³, $Z = 4$, $D_x = 1.641$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu =$

* To whom correspondence should be addressed.