Cs—O3	3.458 (5)	C10—O6	1.423 (6)
Cs—O4	3.510 (5)	O6—C19^{i}	1.394 (6)
Cs—O5	3.192 (4)	O1—C11	1.393 (6)
Cs—O6	3.286 (3)	C11—C12	1.401 (7)
Cs···C13^{i}	3.770 (5)	C11—C16	1.397 (7)
Cs···C14^{i}	3.489 (5)	C12—C13	1.397 (7)
Cs···C15^{i}	3.709 (5)	C12—C25	1.501 (6)
Cs···C21	3.509 (5)	C13—C14	1.386 (8)
Cs···C22	3.273 (5)	C14—C15	1.375 (7)
Cs···C23	3.559 (5)	C15—C16	1.407 (8)
O1—C1	1.449 (6)	C16—C17	1.505 (7)
C1—C2	1.478 (7)	C17—C18	1.524 (7)
C2—O2	1.398 (6)	C18—C19	1.397 (7)
O2—C3	1.405 (7)	C18—C23	1.378 (8)
C3—C4	1.491 (9)	C19—C20	1.394 (7)
C4—O3	1.383 (7)	C20—C21	1.389 (8)
O3—C5	1.45 (1)	C20—C24	1.520 (7)
C5—C6	1.28 (1)	C21—C22	1.393 (8)
C6—O4	1.39 (1)	C22—C23	1.376 (8)
O4—C7	1.355 (8)	N—C26	1.111 (8)
C7—C8	1.437 (9)	C26—C27	1.426 (9)
I—Cs—O1	126.73 (5)	O1—C11—C12	120.2 (5)
I—Cs—O2	91.31 (7)	O1—C11—C16	116.7 (4)
I—Cs—O3	79.99 (9)	C12—C11—C16	123.1 (5)
I—Cs—O4	80.7 (1)	C11—C12—C13	116.8 (5)
I—Cs—O5	85.14 (7)	C11—C12—C25	122.7 (4)
I—Cs—O6	120.22 (6)	C12—C13—C14	121.2 (5)
O1—Cs—O2	53.93 (8)	C13—C12—C25	120.5 (4)
O2—Cs—O3	51.1 (1)	C13—C14—C15	120.7 (5)
O3—Cs—O4	49.4 (1)	C14—C15—C16	120.6 (5)
O4—Cs—O5	49.5 (1)	C15—C16—C11	117.3 (5)
O5—Cs—O6	53.23 (8)	C15—C16—C17	119.9 (5)
C11—O1—C1	113.9 (4)	C11—C16—C17	122.8 (5)
O1—C1—C2	112.2 (4)	C16—C17—C18	115.9 (4)
C1—C2—O2	110.8 (4)	C17—C18—C19	122.7 (5)
C2—O2—C3	112.8 (4)	C17—C18—C23	119.6 (5)
O2—C3—C4	110.6 (5)	C19—C18—C23	117.7 (5)
C3—C4—O3	109.9 (6)	C18—C19—C20	122.0 (5)
C4—O3—C5	111.4 (6)	C19—C20—C21	118.1 (5)
O3—C5—C6	117.0 (9)	C19—C20—C24	122.3 (4)
C5—C6—O4	121.5 (7)	C21—C20—C24	119.6 (5)
C6—O4—C7	116.9 (6)	C20—C21—C22	120.5 (5)
O4—C7—C8	113.4 (6)	C21—C22—C23	119.6 (5)
C7—C8—O5	112.5 (6)	C18—C23—C22	121.8 (5)
C8—O5—C9	114.1 (5)	C12—C25—C12^{i}	115.6 (6)
O5—C9—C10	113.3 (5)	C20—C24—C20^{i}	116.9 (6)
C9—C10—O6	114.1 (5)	N—C26—C27	178.7 (8)
C10—O6—C19^{i}	113.5 (4)		
C12—C11—O1—C1	68.6 (5)	C5—C6—O4—C7	103.6 (8)
C16—C11—O1—C1	−112.0 (4)	C6—O4—C7—C8	164.6 (6)
C11—O1—C1—C2	123.5 (4)	O4—C7—C8—O5	60.9 (7)
O1—C1—C2—O2	69.8 (5)	C7—C8—O5—C9	−179.0 (5)
C1—C2—O2—C3	172.9 (4)	C8—O5—C9—C10	−172.5 (5)
C2—O2—C3—C4	−175.8 (4)	O5—C9—C10—O6	−63.7 (6)
O2—C3—C4—O3	−69.5 (6)	C9—C10—O6—C19^{i}	−125.1 (4)
C3—C4—O3—C5	−173.4 (6)	C10—O6—C19^{i}—C18^{i}	−69.2 (5)
C4—O3—C5—C6	−173.3 (7)	C10—O6—C19^{i}—C20^{i}	110.7 (4)
O3—C5—C6—O4	56 (1)		

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

Data were corrected for Lorentz–polarization effects. The structure was solved using *SHELXS*86 (Sheldrick, 1985) which gave the main part of the structure. Missing atoms were found by subsequent Fourier differences. H atoms were included as riding atoms at calculated positions (C—H = 0.95 Å, B = 6 Å^2). Analytical scattering factors for neutral atoms were corrected for $\Delta f'$ and $\Delta f''$. All calculations were performed on a VAX4000-200 computer.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86. Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1233). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Asfari, Z., Bressot, C., Vicens, J., Hill, C., Dozol, J. F., Rouquette, H., Eymard, S., Lamare, V. & Tournois, B. (1995). *Anal. Chem.* **67**, 3133–3139.

Asfari, Z., Naumann, C., Nierlich, M., Thuéry, P., Bressot, C., Lamare, V., Dozol, J. F. & Vicens, J. (1996). *New J. Chem.* In the press.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.

Fyles, T. M. & Gandour, R. D. (1992). *J. Incl. Phenom.* **12**, 313–332.

Hill, C., Dozol, J. F., Lamare, V., Rouquette, H., Eymard, S., Tournois, B., Vicens, J., Asfari, Z., Bressot, C., Ungaro, R. & Casnati, A. (1994). *J. Incl. Phenom.* **19**, 399–408.

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

Lide, D. R. (1992). Editor. In *Handbook of Chemistry and Physics*, 72nd ed. Boca Raton: CRC Press.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Thuéry, P., Nierlich, M., Bressot, C., Lamare, V., Dozol, J. F., Asfari, Z. & Vicens, J. (1996). *J. Incl. Phenom.* **23**, 305–312.

Thuéry, P., Nierlich, M., Lamare, V., Dozol, J. F., Asfari, Z. & Vicens, J. (1996). *J. Incl. Phenom.* Submitted.

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A Mixed-Metal Pentanuclear Complex Containing Linked Ni^{II}N$_2$S$_2$ and Cu^{I}I Units

STEPHEN FOX, ROBERT T. STIBRANY, JOSEPH A. POTENZA* AND HARVEY J. SCHUGAR

Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, NJ 08903, USA. E-mail: potenza@xstal.rutgers.edu

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Abstract

Bis[(1S,2S)-*trans*-3,3′-(1,2-cyclohexanediyldinitrilo)bis-(2-methylpropane-2-thiolato)]-$1\kappa^4N^1,N^{1'},S^1,S^{1'};2\kappa^4N^2,N^{2'},S^2,S^{2'};3\kappa^2S^1,S^{2'};4\kappa^2S^{1'},S^2;5\kappa^2S^{1'},S^{2'}$-triiodo-$3\kappa I,4\kappa I,5\kappa I$-tricopper(I)dinickel(II) bis(acetonitrile) solvate, [{Ni($C_{14}H_{28}N_2S_2$)}$_2$(CuI)$_3$].2CH$_3$CN, is one of a number of possible novel pentanuclear complexes formed from M^{II}N$_2$S$_2$ units with available donating thiolate ligands. In the title compound, three Cu^{I}I groups bridge

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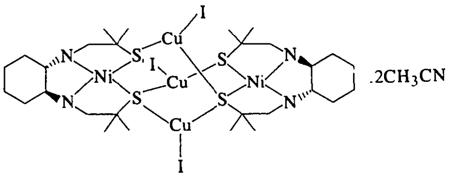
thiolate ligands from two approximately square-planar $[Ni^{II}N(amine)_2S(thiolate)_2]$ units to form the pentanuclear complex. The coordination geometry of each Cu atom is approximately trigonal planar.

Comment

We have been interested in synthesizing models of CuN_2S_2 binding sites in proteins (Bharadwaj, Potenza & Schugar, 1986). During this process, we have found that certain $[M^{II}N(amine)_2S(thiolate)_2]$ units lend themselves to forming novel pentanuclear complexes owing to the availability of potentially bridging thiolate ligands. The first reported example of such a complex contains three approximately planar $[Cu^{II}N(amine)_2S(thiolate)_2]$ units bridged by two Cu^I ions [abbreviated as $(Cu^{II}N_2S_2)_3(Cu^I)_2$] [(2); Bharadwaj, John, Xie, Zhang, Hendrickson, Potenza & Schugar, 1986]. Recently, an example of a mixed-metal pentanuclear complex involving $Zn^{II}Cl$ as the bridging group, $[(Ni^{II}N_2S_2)_3(Zn^{II}Cl)_2]$, has been reported [(3); Tuntulani, Reibenspies, Farmer & Darensbourg, 1992]. The (−) optical configuration of one of the N_2S_2 ligands, (1*S*,2*S*)-*trans*-3,3′-(1,2-cyclohexanediyldinitrilo)bis(2-methylpropane-2-thiolate), has been determined as part of the study of a complex containing the $[(Cu^{II}N_2S_2)_3(Cu^ICu^ICl)]$ nucleus (Brader, Stibrany, Potenza & Schugar, 1996).



(I)

Complex (1) contains two $Ni^{II}N_2S_2$ units bridged by three μ-Cu^II moieties. Bond distances and angles within the N_2S_2 ligands compare favorably to those in a monomeric $Zn^{II}N_2S_2$ complex, (4), which contains the same ligand (Potenza, Stibrany, Potenza & Schugar, 1992). The Ni—N and Ni—S bond distances in (1) agree favorably with those reported for (3) and are *ca.* 0.1 Å shorter than the corresponding Zn—N/S distances in (4), in accordance with the difference in ionic radii between Zn^{II} and Ni^{II}. Complex (1) provides the first example of a structure in which a μ-Cu^II unit bridges two thiolate atoms. A structure has been reported in which a Cu^II unit bridges methylthio S atoms [(5); Brunn, Endres & Weiss, 1988], but in that structure the I atoms also bridge two Cu atoms to form a polymeric species in the solid state. The Cu^I—S bond distances compare favorably to those reported for (2) [2.237 (5)–2.266 (4) Å]. Coordination about the Cu atom is distorted trigonal planar. The Cu1 atom shows the smallest deviation from its IS_2 plane [0.0951 (9) Å]; for the Cu2 and Cu3 atoms, the corresponding deviations are 0.234 (1) and 0.255 (1) Å, respectively. Coordination about nickel is distorted square planar, as expected. A measure of the distortion from square-planar towards tetrahedral coordination is given by the NiS_2/NiN_2 dihedral angles, which are 15.7 (5) and 15.1 (6)° for Ni1 and Ni2, respectively. These distortions are smaller than those found for related Cu^{II} complexes [21.0 (6) and 32.77 (6)°; Potenza, Stibrany, Potenza & Schugar, 1992], reflecting the stronger tendency for d^8 Ni^{II} to form square-planar complexes.

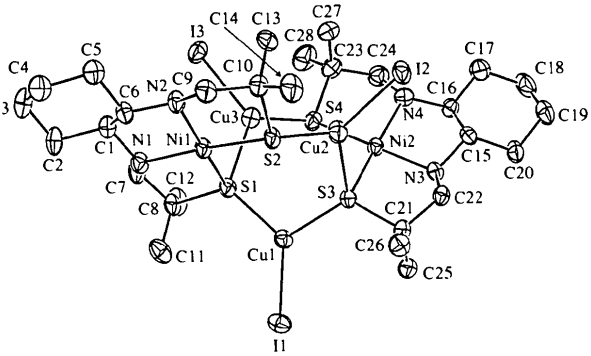


Fig. 1. View of complex (1) (*ORTEP*II; Johnson, 1976) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 35% level. H atoms and lattice acetonitrile molecules have been omitted for clarity.

Experimental

Black crystals of (1) were obtained by slow evaporation of an acetonitrile solution of a 3:2 mixture of Cu^II and $NiN_2S_2C_{14}H_{28}$. The density D_m was measured by flotation in a mixture of carbon tetrachloride and 1,2-dibromoethane.

Crystal data

$[Cu_3Ni_2I_3(C_{14}H_{28}N_2S_2)_2]$.-
$2C_2H_3N$
$M_r = 1343.87$
Triclinic
$P\bar{1}$
$a = 12.837\ (3)$ Å
$b = 18.081\ (4)$ Å
$c = 11.747\ (4)$ Å
$\alpha = 96.49\ (2)°$
$\beta = 106.84\ (3)°$
$\gamma = 107.77\ (3)°$
$V = 2422.0$ Å^3
$Z = 2$
$D_x = 1.843$ Mg m^{-3}
$D_m = 1.84\ (1)$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.93$–$16.82°$
$\mu = 4.16$ mm^{-1}
$T = 298$ K
Prism
0.50 × 0.12 × 0.04 mm
Black

Data collection

Enraf–Nonius CAD-4 diffractometer

4724 observed reflections [$I > 3\sigma(I)$]

$\theta/2\theta$ scans
Absorption correction:
ψ scan (*SDP*; Enraf–Nonius, 1985)
$T_{\min} = 0.67$, $T_{\max} = 0.85$
5933 measured reflections
5933 independent reflections

$\theta_{\max} = 22°$
$h = 0 \rightarrow 13$
$k = -18 \rightarrow 18$
$l = -12 \rightarrow 11$
3 standard reflections
monitored every 300 reflections
intensity decay: 4.1%

Refinement

Refinement on F
$R = 0.0388$
$wR = 0.047$
$S = 1.60$
4724 reflections
451 parameters
H atoms: see below
$w = 4F^2/[\sigma^2(F^2) + 0.0016F^4]$

$(\Delta/\sigma)_{\max} = 0$
$\Delta\rho_{\max} = 1.603$ e Å^{-3}
$\Delta\rho_{\min} = -0.151$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$B_{\rm eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
I1	−0.28551 (4)	0.01678 (3)	−0.12310 (5)	4.31 (1)
I2	0.14239 (5)	0.48794 (3)	0.28152 (5)	4.58 (1)
I3	0.10746 (4)	0.21067 (3)	0.60060 (4)	4.40 (1)
Cu1	−0.12773 (7)	0.12876 (5)	0.03861 (7)	3.35 (2)
Cu2	0.08364 (8)	0.33859 (5)	0.21794 (9)	4.48 (3)
Cu3	0.00611 (8)	0.20467 (5)	0.37623 (8)	4.38 (2)
Ni1	0.17693 (7)	0.16473 (5)	0.31387 (7)	2.76 (2)
Ni2	−0.15492 (7)	0.32202 (5)	0.17826 (7)	3.00 (2)
S1	−0.0075 (1)	0.1140 (1)	0.2106 (2)	2.98 (4)
S2	0.2109 (2)	0.2765 (1)	0.2570 (2)	3.66 (5)
S3	−0.0867 (2)	0.2611 (1)	0.0647 (2)	3.26 (4)
S4	−0.1342 (2)	0.2550 (1)	0.3183 (2)	3.45 (4)
N1	0.1685 (4)	0.0629 (3)	0.3537 (5)	2.8 (1)
N2	0.3267 (5)	0.2082 (3)	0.4380 (5)	3.6 (2)
N3	−0.2060 (5)	0.3741 (3)	0.0500 (5)	3.6 (1)
N4	−0.1879 (5)	0.3954 (3)	0.2811 (5)	3.5 (1)
C1	0.2634 (6)	0.0756 (4)	0.4700 (6)	3.2 (2)
C2	0.2953 (6)	0.0026 (4)	0.4929 (7)	4.1 (2)
C3	0.3955 (6)	0.0238 (5)	0.6124 (7)	4.9 (2)
C4	0.5013 (7)	0.0914 (5)	0.6126 (8)	6.0 (3)
C5	0.4709 (7)	0.1647 (5)	0.5870 (8)	4.9 (2)
C6	0.3698 (6)	0.1431 (4)	0.4690 (6)	3.5 (2)
C7	0.0519 (5)	0.0157 (4)	0.3535 (6)	3.0 (2)
C8	−0.0418 (5)	0.0107 (4)	0.2364 (6)	3.0 (2)
C9	0.4092 (6)	0.2768 (5)	0.4153 (7)	4.6 (2)
C10	0.3521 (6)	0.3367 (4)	0.3790 (7)	4.1 (2)
C11	−0.0414 (6)	−0.0440 (4)	0.1288 (7)	3.9 (2)
C12	−0.1596 (6)	−0.0147 (5)	0.2529 (7)	4.2 (2)
C13	0.3366 (7)	0.3806 (5)	0.4866 (8)	5.0 (2)
C14	0.4256 (8)	0.3958 (5)	0.323 (1)	6.6 (3)
C15	−0.2176 (6)	0.4484 (4)	0.1028 (7)	3.8 (2)
C16	−0.2644 (6)	0.4306 (4)	0.2038 (6)	3.6 (2)
C17	−0.2770 (6)	0.5043 (5)	0.2703 (7)	4.4 (2)
C18	−0.3533 (7)	0.5353 (5)	0.1791 (8)	5.4 (2)
C19	−0.3062 (7)	0.5539 (5)	0.0772 (8)	5.8 (2)
C20	−0.2912 (7)	0.4831 (4)	0.0112 (7)	5.0 (2)
C21	−0.1216 (6)	0.3045 (4)	−0.0718 (6)	3.6 (2)
C22	−0.1332 (6)	0.3827 (4)	−0.0287 (6)	4.2 (2)
C23	−0.1425 (6)	0.3239 (4)	0.4428 (6)	3.6 (2)
C24	−0.2226 (6)	0.3646 (4)	0.3815 (6)	4.0 (2)
C25	−0.2350 (7)	0.2479 (5)	−0.1667 (7)	5.5 (2)
C26	−0.0219 (7)	0.3191 (5)	−0.1205 (7)	5.5 (2)
C27	−0.0238 (7)	0.3814 (5)	0.5198 (6)	4.3 (2)
C28	−0.1993 (7)	0.2735 (5)	0.5204 (7)	5.2 (2)
N5	0.4870 (9)	0.7234 (8)	0.071 (1)	13.7 (5)
C29	0.574 (1)	0.7429 (7)	0.055 (1)	9.7 (4)
C30	0.686 (1)	0.7697 (8)	0.035 (1)	10.3 (4)
N6	0.4735 (9)	0.7944 (7)	0.781 (1)	17.3 (4)
C31	0.4472 (9)	0.8347 (8)	0.834 (1)	10.3 (4)
C32	0.4127 (9)	0.8893 (7)	0.903 (1)	11.3 (4)

Table 2. *Selected geometric parameters (Å, °)*

I1—Cu1	2.4925 (8)	Ni1—S1	2.163 (2)
I2—Cu2	2.528 (1)	Ni1—S2	2.156 (2)
I3—Cu3	2.552 (1)	Ni1—N1	1.928 (6)
Cu1—S1	2.259 (2)	Ni1—N2	1.907 (5)
Cu1—S3	2.250 (2)	Ni2—S3	2.166 (2)
Cu2—S2	2.223 (2)	Ni2—S4	2.152 (2)
Cu2—S3	2.295 (2)	Ni2—N3	1.926 (6)
Cu3—S1	2.327 (2)	Ni2—N4	1.917 (7)
Cu3—S4	2.228 (2)		
I1—Cu1—S1	124.64 (6)	S1—Ni1—N2	166.1 (2)
I1—Cu1—S3	130.41 (6)	S2—Ni1—N1	169.5 (2)
S1—Cu1—S3	104.44 (6)	S2—Ni1—N2	88.9 (2)
I2—Cu2—S2	122.77 (5)	N1—Ni1—N2	87.2 (2)
I2—Cu2—S3	122.54 (7)	S3—Ni2—S4	96.21 (9)
S2—Cu2—S3	111.74 (8)	S3—Ni2—N3	89.9 (2)
I3—Cu3—S1	126.12 (7)	S3—Ni2—N4	167.8 (2)
I3—Cu3—S4	121.51 (7)	S4—Ni2—N4	89.6 (2)
S1—Cu3—S4	108.90 (7)	N3—Ni2—N4	86.3 (3)
S1—Ni1—S2	97.26 (8)	S4—Ni2—N3	168.4 (2)
S1—Ni1—N1	88.7 (1)		

The title structure was solved by direct methods (*MULTAN*11/82; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and difference Fourier techniques. The refinement was by full-matrix least squares on F. H atoms were found from difference Fourier maps and calculated positions, and were not refined. The largest three peaks on the final difference Fourier map were residuals of I1, I3 and I2.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MULTAN*11/82. Program(s) used to solve structure: *MULTAN*11/82. Program(s) used to refine structure: *MULTAN*11/82. Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1057). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bharadwaj, P. K., John, E., Xie, C.-L., Zhang, D., Hendrickson, D. N., Potenza, J. A. & Schugar, H. J. (1986). *Inorg. Chem.* **25**, 4541–4546.

Bharadwaj, P. K., Potenza, J. A. & Schugar, H. J. (1986). *J. Am. Chem. Soc.* **108**, 1351–1352.

Brader, M. L., Stibrany, R. T., Potenza, J. A. & Schugar, H. J. (1996). In preparation.

Brunn, K., Endres, H. & Weiss, J. (1988). *Z. Naturforsch. Teil B*, **43**, 224–230.

Enraf–Nonius (1985). *Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.

Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Universities of York, England, and Louvain, Belgium.
Potenza, M. N., Stibrany, R. T., Potenza, J. A. & Schugar, H. J. (1992). *Acta Cryst.* C**48**, 454–457.
Tuntulani, T., Reibenspies, J. H., Farmer, P. J. & Darensbourg, M. Y. (1992). *Inorg. Chem.* **31**, 3497–3499.

Acta Cryst. (1996). C**52**, 2734–2736

Tris{2-[(4-chlorophenyl)iminomethyl]pyrrolato-*N*,*N*′}cobalt(III)

J. A. Castro, J. Romero, J. A. García-Vázquez, A. Sousa* and A. Castiñeiras

Departamento de Química Inorgánica, Universidade de Santiago de Compostela, E-15706 Santiago de Compostela, Spain. E-mail: qiac01@usc.es

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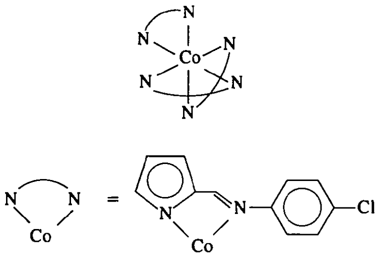
Abstract

The title compound, $[Co(C_{11}H_8ClN_2)_3]$, consists of monomeric molecules in which the central CoN_6 unit has slightly distorted octahedral geometry, with bond lengths ranging from 1.900 (8) to 1.991 (7) Å. In the complex, the ligands adopt positions such that the complex can be described as the meridional isomer.

Comment

Metal complexes with Schiff base ligands containing weak acid groups can be satisfactorily synthesized following an electrochemical procedure similar to that described by Oldham & Tuck (1982). Starting from metallic cobalt as the anode of an electrochemical cell containing the Schiff base dissolved in acetonitrile, the title compound, (I), was obtained.



(I)

The Co atom is coordinated to three bidentate anionic ligands; the environment around the metal atom can be described as having slightly distorted octahedral geometry, with the angles defined by two *trans*-N atoms close to the expected value of 180° [177.8 (3), 174.7 (3) and 174.8 (3)°] and the angles determined by the Co and two *cis*-N atoms close to 90° (Fig. 1). The Co—N(pyrrole) bond distances [average 1.911 (8) Å] are shorter than the Co—N(azomethine) bond distances [average 1.965 (7) Å]. These values are similar to those of the corresponding bonds found in cobalt(III) complexes with similar ligands (Castro *et al.*, 1992). In the title complex, the ligands adopt positions such that the complex can be described as the meridional isomer. Three signals in the ^{1}H NMR spectrum at 7.73, 7.62 and 7.59 p.p.m., attributable to the three non-equivalent imine protons, indicate that this coordination is maintained in solution. In the complex, the chelate Co—N—C—C—N rings are almost planar, the maximum deviation being 0.053 Å, and the bond distances and angles of these rings are as expected; in particular, the average value of the C—N bond length [1.31 (2) Å] is typical for a C=N bond. Although the three ligands are very similar in terms of their bond distances and angles and the pyrrole and phenol rings are planar, the angles between the planes are 56.6 (4), 77.6 (4) and 56.6 (4) in ligands *A* (N11 and N12 donor atoms), *B* (N21 and N22 donor atoms) and *C* (N31 and N32 donor atoms), respectively. The angles between the planes of each pyrrole ring and the plane composed of atoms Co, N11, N12, N22 and N31 are 7.75 (4), 81.4 (4) and 82.5 (4)° for ligands *A*, *B* and *C*, respectively; the pyrrole ring of ligand *A* is thus almost coplanar with this coordination plane, while the pyrrole rings of the *B* and *C* ligands are almost perpendicular to it. It is interesting to note that only the *A* ligand can influence the *fac*/*mer* isomerization (by exchange of N-atom positions).

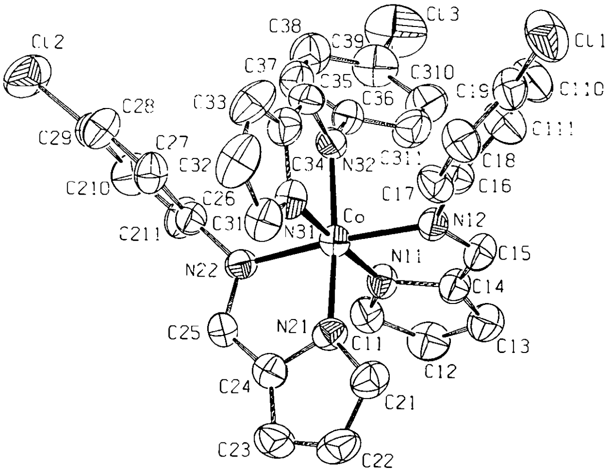


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.