

P(3)	-0.5043 (2)	-0.3443 (1)	-0.0797 (1)	0.0333 (6)
N(3)	-0.5108 (7)	-0.2550 (3)	-0.1155 (3)	0.0348 (20)
N(11)	-0.2633 (7)	-0.1483 (3)	-0.1140 (3)	0.0381 (22)
C(12)	-0.2699 (9)	-0.0885 (5)	-0.1821 (4)	0.0469 (25)
C(13)	-0.3825 (17)	-0.0206 (7)	-0.1755 (7)	0.1103 (60)
C(14)	-0.4657 (12)	-0.0216 (4)	-0.1019 (6)	0.0561 (32)
N(15)	-0.5306 (7)	-0.1012 (3)	-0.0897 (4)	0.0406 (20)
N(21)	-0.4161 (8)	-0.2586 (4)	0.1608 (3)	0.0438 (22)
C(22)	-0.5680 (12)	-0.2134 (7)	0.1489 (6)	0.0872 (46)
C(23)	-0.3950 (13)	-0.3139 (5)	0.2326 (5)	0.0698 (38)
N(31)	-0.1708 (8)	-0.3188 (4)	0.1090 (4)	0.0474 (22)
C(32)	-0.1157 (16)	-0.3916 (9)	0.0796 (9)	0.1316 (63)
C(33)	-0.0540 (12)	-0.2644 (6)	0.1573 (6)	0.0805 (40)
N(41)	-0.3910 (9)	-0.3983 (4)	-0.1299 (4)	0.0520 (22)
C(42)	-0.3768 (16)	-0.4855 (5)	-0.1155 (7)	0.0823 (50)
C(43)	-0.2998 (11)	-0.3685 (5)	-0.1891 (5)	0.0648 (35)
N(51)	-0.6780 (7)	-0.3895 (4)	-0.1009 (4)	0.0454 (22)
C(52)	-0.7980 (11)	-0.3637 (6)	-0.0520 (6)	0.0695 (37)
C(53)	-0.7379 (14)	-0.4070 (6)	-0.1887 (6)	0.0861 (44)

Table 2. Selected geometric parameters (Å, °)

Pt(1)—Cl(1)	2.308 (2)	P(3)—N(3)	1.590 (5)	
Pt(1)—Cl(2)	2.318 (2)	P(1)—N(11)	1.615 (6)	
P(1)—N(1)	1.678 (5)	P(1)—N(15)	1.609 (6)	
P(1)—N(3)	1.567 (5)	P(2)—N(21)	1.630 (6)	
N(1)—P(2)	1.670 (5)	P(2)—N(31)	1.640 (7)	
P(2)—N(2)	1.555 (5)	P(3)—N(41)	1.632 (8)	
N(2)—P(3)	1.602 (5)	P(3)—N(51)	1.644 (6)	
Cl(1)—Pt(1)—Cl(2)	90.84 (7)	N(21)—P(2)—N(31)	104.3 (3)	
N(11)—P(1)—N(15)	101.8 (3)	P(2)—N(2)—P(3)	126.2 (4)	
N(1)—P(1)—N(3)	108.7 (3)	N(2)—P(3)—N(3)	113.2 (3)	
P(1)—N(1)—P(2)	127.7 (3)	N(41)—P(3)—N(51)	103.4 (4)	
N(1)—P(2)—N(2)	111.0 (3)	P(1)—N(3)—P(3)	128.3 (3)	
P(1)—N(11)—C(12)	124.1 (5)	P(1)—N(15)—C(14)	120.8 (6)	
D—H...A	D—H	H...A	D...A	D—H...A
N(1)—H1...Cl(1)	0.81 (7)	2.56 (7)	3.363 (5)	172 (6)
N(11)—H11...Cl(2)	0.82 (7)	2.60 (7)	3.332 (6)	148 (6)
N(15)—H15...Cl(2)	0.86 (7)	2.74 (8)	3.533 (7)	154 (7)

Symmetry code: (i) $x - 1, y, z$.

Table 3. Observed trends in the ring angles (°) of cyclotriphosphazene derivatives

	Cyclotri-phosphazenes	Cyclotri-phosphazene complexes*	Protonated salts and phosphazadienes
Mean ring N—P—N angle	119.4–116.7	116.0–114.0	112.0–110.0
Mean ring P—N—P angle	119.3–123.0	122.7–125.0	125.0–128.7
No. of structures	30	8	6

* Only when a ring N atom is involved in coordination; if it is weaker than a normal metal–nitrogen bond, the values fall within the ranges for cyclotriphosphazenes.

Data collection and cell refinement: *CAD-4 Software* (Enraf–Nonius, 1989). Data reduction: *DRDACS* (Chandrasekaran, 1990). Structure solution (Patterson heavy-atom method) and refinement: *SHELX76* (Sheldrick, 1976). All non-H atoms were refined anisotropically; 27 of 33 H atoms were located from $\Delta\rho$ synthesis and were refined isotropically, other H atoms were not included in the calculations. Bond parameter calculations: *PARST* (Nardelli, 1983). All calculations were carried out on a VAX8810 computer.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances involving H atoms and bond angles involving non-H atoms have been deposited with the IUCr (Reference: AB1134). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Allcock, H. R., Bissell, E. C. & Shawl, E. T. (1973). *Inorg. Chem.* **12**, 2963–2968.
- Allcock, H. R., Desorcie, J. L. & Riding, G. H. (1987). *Polyhedron*, **6**, 119–157.
- Calhoun, H. P. & Trotter, J. (1974a). *J. Chem. Soc. Dalton Trans.* pp. 377–381.
- Calhoun, H. P. & Trotter, J. (1974b). *J. Chem. Soc. Dalton Trans.* pp. 382–386.
- Chandrasekaran, A. (1990). *DRDACS. Program for X-ray Data Reduction*. Indian Institute of Science, Bangalore, India.
- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- MacDonald, A. L. & Trotter, J. (1974). *Can. J. Chem.* **52**, 734–737.
- Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
- O'Brien, J. P., Allen, R. W. & Allcock, H. R. (1979). *Inorg. Chem.* **18**, 2230–2235.
- Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.
- Trotter, J. & Whitlow, S. H. (1970). *J. Chem. Soc. A*, pp. 460–464.
- Ugozzoli, F. (1987). *Comput. Chem.* **11**, 109–120.

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{Tris[N-(salicylidene)-2-aminoethyl]-amine}cobalt(III) Acetonitrile Hemihydrate

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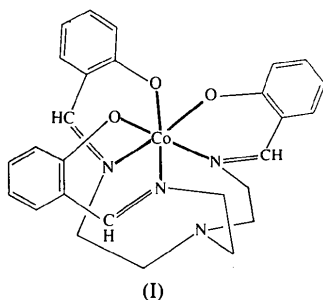
Abstract

The slightly distorted octahedral coordination sphere of cobalt in {2,2',2''-[nitrilotris(ethylenenitrilomethylidene- κ N)]triphenolato- κ^3 O}cobalt(III) acetonitrile hemihydrate, [Co(C₂₇H₂₇N₄O₃)]₂.CH₃CN.0.5H₂O, is formed from three N and three O atoms which are in a *fac* arrangement. The chelate rings formed by the salicylidene–imine moieties are almost planar [maximum deviation of the Co atom from a least-squares

plane calculated for the atoms of a salicylidene-imine moiety is 0.101 (4) Å. Average bond lengths are 1.893 (3) Å for Co—O and 1.947 (4) Å for Co—N.

Comment

Complexes of transition metal ions with Schiff bases are becoming an increasingly large class of compounds of both stereochemical and magnetochemical interest. Recently, structural and molecular properties of related Co^{III} complexes were reported (Koziol, Palenik & Palenik 1986; Gatehouse, Martin, McLachlan, Platts & Spiccia, 1992; Attia, Zangrando, Randaccio, Antolini & Lopez, 1989). In the title compound, (I), cobalt is surrounded by three N and three O atoms which form a slightly distorted *fac*-octahedral coordination geometry. The average Co—O [1.893 (3) Å] and Co—N [1.947 (4) Å] bond lengths are in agreement with those found by Koziol *et al.* (1986). The central amine N atom of the tris(2-aminoethyl)amine moiety does not coordinate to the Co atom.



Average bond angles are 170.7 (2) (O—Co—N), 89.7 (2) (*cis*-O—Co—N), 85.8 (1) (O—Co—O) and 94.8 (2)° (N—Co—N). The asymmetric unit of the structure comprises one molecule of the Co complex, one acetonitrile molecule and half a water molecule, which is disordered over a centre of symmetry.

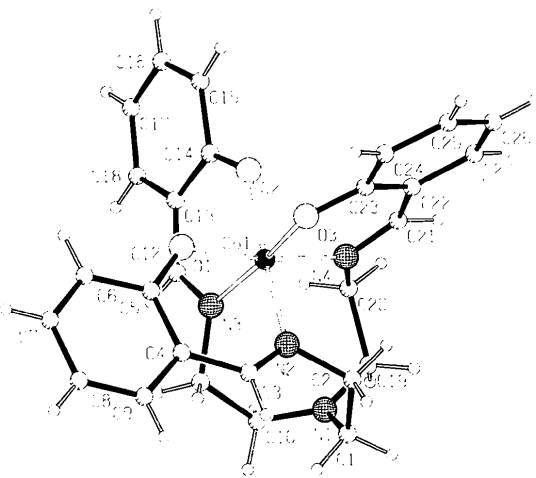


Fig. 1. PLUTON (Spek, 1993) plot of the structure of the title complex.

Experimental

The title compound was prepared by adding 1 mmol cobalt(II) acetate tetrahydrate dissolved in 20 ml methanol to a solution of 1 mmol tris[*N*-(salicylidene)-2-aminoethyl]amine (trensal) in 50 ml acetonitrile containing 0.1 mol piperidine. Refluxing the mixture for 4 d yielded the title compound as dark red prismatic crystals.

Crystal data

[Co(C₂₇H₂₇N₄O₃)]·CH₃CN·
0.5H₂O

M_r = 564.53

Orthorhombic

Pbca

a = 13.027 (3) Å

b = 16.619 (6) Å

c = 23.942 (4) Å

V = 5422.1 (25) Å³

Z = 8

D_x = 1.383 Mg m⁻³

Mo *Kα* radiation

λ = 0.71069 Å

Cell parameters from 25 reflections

θ = 2.25–15.02°

μ = 0.670 mm⁻¹

T = 301 (2) K

Prism

0.45 × 0.25 × 0.10 mm

Dark red

Data collection

Enraf–Nonius CAD-4
diffractometer

ω/2θ scans

Absorption correction:

empirical

T_{min} = 0.734, *T_{max}* =

0.911

7086 measured reflections

3762 independent reflections

2489 observed reflections

[*I* > 2σ(*I*)]

R_{int} = 0.0435

θ_{max} = 22.97°

h = -14 → 14

k = -18 → 18

l = -26 → 26

3 standard reflections

frequency: 120 min

intensity variation: 2.1%

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.051

wR(*F*²) = 0.132

S = 1.115

3757 reflections

364 parameters

w = 1/[σ²(*F_o*²) + (0.0880*P*)²

+ 2.6556*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = -0.43

Δρ_{max} = 0.73 e Å⁻³

Δρ_{min} = -0.27 e Å⁻³

Atomic scattering factors

from *International Tables for Crystallography* (1992),

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Co1	0.11890 (4)	0.89206 (4)	0.15663 (2)	0.0371 (2)
O1	0.0966 (2)	0.7921 (2)	0.19211 (13)	0.0439 (8)
O2	0.1052 (2)	0.8328 (2)	0.08962 (13)	0.0484 (9)
O3	-0.0196 (2)	0.9033 (2)	0.15504 (13)	0.0453 (8)
N1	0.2875 (3)	1.0450 (3)	0.1935 (2)	0.0565 (12)
N2	0.1088 (3)	0.9535 (2)	0.2253 (2)	0.0394 (9)
N3	0.2577 (3)	0.8689 (2)	0.16593 (15)	0.0410 (10)
N4	0.1424 (3)	0.9843 (2)	0.1074 (2)	0.0446 (10)
C1	0.2144 (4)	1.0730 (3)	0.2335 (2)	0.0585 (14)
C2	0.1104 (4)	1.0420 (3)	0.2252 (2)	0.0481 (13)
C3	0.0929 (3)	0.9218 (3)	0.2736 (2)	0.0403 (12)
C4	0.0909 (3)	0.8384 (3)	0.2870 (2)	0.0390 (11)
C5	0.0932 (3)	0.7775 (3)	0.2459 (2)	0.0385 (11)
C6	0.0918 (4)	0.6970 (3)	0.2634 (2)	0.0479 (12)

C7	0.0898 (4)	0.6780 (3)	0.3188 (2)	0.0552 (14)
C8	0.0879 (4)	0.7366 (4)	0.3594 (2)	0.0583 (15)
C9	0.0872 (4)	0.8157 (3)	0.3439 (2)	0.0506 (13)
C10	0.3537 (4)	0.9821 (3)	0.2076 (2)	0.0527 (14)
C11	0.3132 (3)	0.8979 (3)	0.2152 (2)	0.0463 (13)
C12	0.3056 (4)	0.8222 (3)	0.1331 (2)	0.0462 (12)
C13	0.2712 (4)	0.7845 (3)	0.0832 (2)	0.0464 (13)
C14	0.1722 (4)	0.7901 (3)	0.0656 (2)	0.0477 (13)
C15	0.1460 (5)	0.7446 (4)	0.0171 (2)	0.065 (2)
C16	0.2150 (6)	0.7011 (4)	-0.0107 (2)	0.081 (2)
C17	0.3116 (6)	0.6988 (4)	0.0051 (2)	0.078 (2)
C18	0.3386 (5)	0.7389 (4)	0.0517 (2)	0.066 (2)
C19	0.2816 (4)	1.0730 (4)	0.1368 (2)	0.064 (2)
C20	0.2419 (4)	1.0126 (3)	0.0942 (2)	0.0542 (14)
C21	0.0729 (4)	1.0176 (3)	0.0794 (2)	0.0442 (12)
C22	-0.0298 (3)	1.0057 (3)	0.0846 (2)	0.0411 (12)
C23	-0.0708 (3)	0.9496 (3)	0.1223 (2)	0.0386 (11)
C24	-0.1739 (4)	0.9443 (3)	0.1247 (2)	0.0490 (13)
C25	-0.2323 (4)	0.9935 (3)	0.0920 (2)	0.0565 (15)
C26	-0.1916 (4)	1.0473 (3)	0.0549 (2)	0.0593 (15)
C27	-0.0920 (4)	1.0523 (3)	0.0514 (2)	0.0498 (13)
N5	0.0489 (6)	0.0834 (7)	0.3735 (4)	0.159 (4)
C28	0.0736 (8)	0.1542 (8)	0.3688 (4)	0.125 (4)
C29	0.1172 (8)	0.2254 (6)	0.3589 (5)	0.143 (4)
O4	0.4896 (14)	0.9588 (10)	0.0245 (7)	0.198 (7)

Table 2. Selected geometric parameters (Å, °)

Co1—O1	1.891 (3)	N1—C10	1.422 (6)
Co1—O2	1.891 (3)	N1—C19	1.436 (7)
Co1—O3	1.897 (3)	N1—C1	1.460 (7)
Co1—N2	1.940 (4)	N2—C3	1.289 (6)
Co1—N3	1.943 (4)	N2—C2	1.471 (6)
Co1—N4	1.959 (4)	N3—C12	1.283 (6)
O1—C5	1.312 (6)	N3—C11	1.482 (6)
O2—C14	1.291 (6)	N4—C21	1.286 (6)
O3—C23	1.302 (5)	N4—C20	1.470 (6)
O1—Co1—O2	84.71 (14)	C5—O1—Co1	127.5 (3)
O1—Co1—O3	86.28 (13)	C14—O2—Co1	126.4 (3)
O2—Co1—O3	86.33 (14)	C23—O3—Co1	127.1 (3)
O1—Co1—N2	94.03 (15)	C10—N1—C19	119.9 (5)
O2—Co1—N2	170.27 (15)	C10—N1—C1	120.7 (5)
O3—Co1—N2	83.96 (15)	C19—N1—C1	118.7 (4)
O1—Co1—N3	86.03 (15)	C3—N2—C2	114.3 (4)
O2—Co1—N3	95.16 (15)	C3—N2—Co1	123.9 (3)
O3—Co1—N3	172.00 (15)	C2—N2—Co1	121.6 (3)
N2—Co1—N3	94.4 (2)	C12—N3—C11	115.1 (4)
O1—Co1—N4	169.7 (2)	C12—N3—Co1	123.0 (3)
O2—Co1—N4	85.0 (2)	C11—N3—Co1	121.6 (3)
O3—Co1—N4	94.24 (15)	C21—N4—C20	115.5 (4)
N2—Co1—N4	96.3 (2)	C21—N4—Co1	122.0 (4)
N3—Co1—N4	93.7 (2)	C20—N4—Co1	122.0 (3)

H atoms were positioned geometrically except for three which were found from a difference synthesis. Water H atoms were excluded from all calculations.

Data collection: Enraf–Nonius *SDP-Plus* (Frenz, 1985). Cell refinement: Enraf–Nonius *SDP-Plus*. Data reduction: *REDU4* (Stoe & Cie, 1988). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *PLUTON93* (Spek, 1993). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: MU1118). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Attia, W. M., Zangrando, E., Randaccio, L., Antolini, L. & Lopez, C. (1989). *Acta Cryst.* **C45**, 1500–1503.
- Frenz, B. A. (1985). *Enraf–Nonius SDP-Plus Structure Determination Package*. Version 3.0. Enraf–Nonius, Delft, The Netherlands.
- Gatehouse, B. M., Martin, R. L., McLachlan, G., Platts, S. N. & Spiccia, L. (1992). *Acta Cryst.* **C48**, 271–274.
- Kozioł, A. E., Palenik, R. C. & Palenik, G. J. (1986). *Inorg. Chem.* **25**, 4461–4462.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.
- Spek, A. L. (1993). *PLUTON93. Program for the Display and Analysis of Crystal and Molecular Structures*. Univ. of Utrecht, The Netherlands.
- Stoe & Cie (1988). *REDU4. Data Reduction Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.

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[2,3-Di(2-pyridyl)pyrazine-*N*¹,*N*²]bis-(triphenylphosphine)copper(I) Nitrate Ethanol Solvate

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Abstract

The copper(I) complex [Cu(C₁₄H₁₀N₄)(C₁₈H₁₅P)₂](NO₃)·C₂H₆O, has been synthesized and its structure determined. The coordination geometry about the Cu atom is distorted tetrahedral with bidentate chelation to dpp, where dpp is 2,3-di(2-pyridyl)pyrazine, and monodentate coordination to two triphenylphosphine ligands.

Comment

The bridging ligand 2,3-di(2-pyridyl)pyrazine (dpp) has been used to prepare luminescent mono- and bimetallic complexes of ruthenium(II) and rhenium(I) (Berger, 1990; Braunstein, Baker, Streckas & Gafney, 1984; Ruminiski & Cambron, 1990). However, until recently, structural information for complexes of these transition metals with dpp had not been reported (Lee, Kirschbaum, Berger & Kirchoff, 1994). We have initiated research to synthesize and examine the luminescence properties of heterobimetallic complexes of