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[*N*,*N'*-1,3-Propylenebis(salicylaldimine)]-bis(pyridine)cobalt(III) Tetraphenylborate Pyridine Solvate

Dun-Ru Zhu,[a]† Xiao-Zeng You,[a] Xiao-Hui Shi,[a]
Hoong-Kun Fun[b] and Kandasamy Sivakumar[b]‡

[a]*Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Centre for Advanced Studies in Science and Technology of Microstructures, Nanjing University, Nanjing 210093, People's Republic of China, and* [b]*X-ray Crystallography Laboratory, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia. E-mail: hkfun@usm.my*

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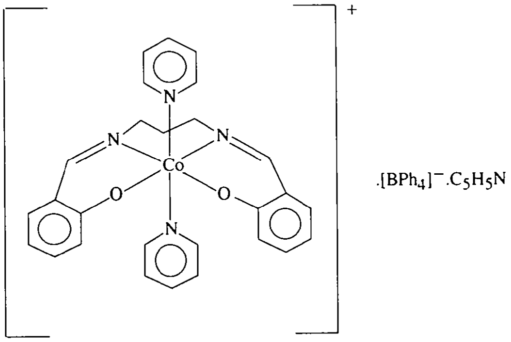
Abstract

The crystal structure determination of the title compound, $[Co(C_{17}H_{16}N_2O_2)(C_5H_5N)_2](C_{24}H_{20}B).C_5H_5N$, indicates that the Co ion has an octahedral environment. The Schiff base ligand {systematic name: 2,2'-[1,3-propanediylbis(nitrilomethylidyne)]diphenolato} is found to be disordered at positions C8 and C9 in the propylene chain.

Comment

Quadridentate Schiff base cobalt complexes have been studied intensively. Their abilities to form stable organometallic derivatives, to bind, reversibly, molecular oxygen and carbon dioxide to the metal centre, and to act as a complex ligand for alkali metal ions and other metallic elements, have been widely investigated (Calligaris, Nardin & Randaccio, 1972; Crumblis & Bosolo, 1970; Floriani & Fachinetti, 1974).



(I)

Recently, some crystal structures have been determined for the free quadridentate ligands (Elerman, Svoboda & Fuess, 1991; Pahor *et al.*, 1976) and their cobalt(II) derivatives in order to obtain insight into the bonding between cobalt and macrocyclic ligands. Since some Co^{II} complexes are air-sensitive, we selected Co^{III} systems for our studies. We report herein the X-ray structure of *trans*-$[Co^{III}(salpron)(py)_2][BPh_4]py$, (I) [salpron = *N*,*N*-1,3-propylenebis(salicylaldimine), py = pyridine]. Fig. 1 shows a displacement ellipsoid plot of the complex molecule with the numbering scheme.

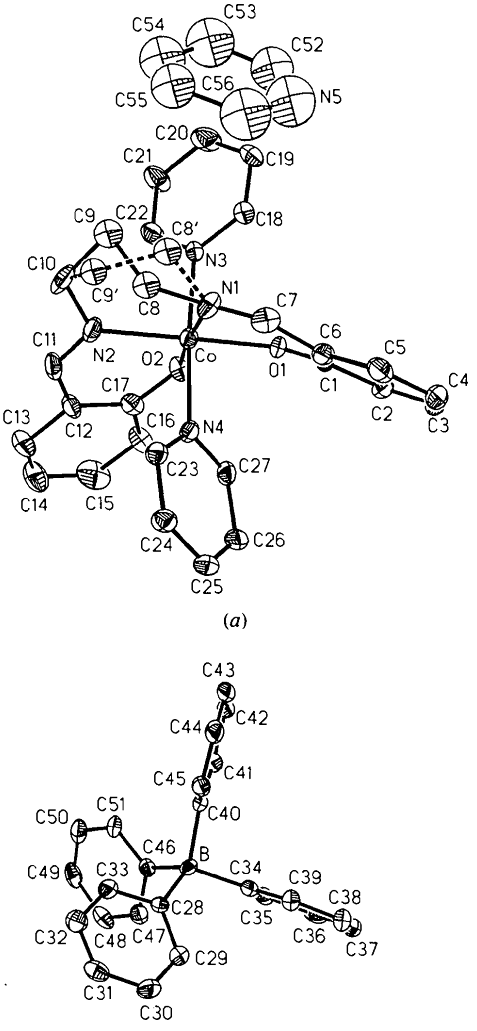


Fig. 1. A displacement ellipsoid (30% probability) plot with the numbering scheme of (*a*) the complex and solvent, and (*b*) the anion.

The axial Co—N(py) bond lengths [Co—N3 1.963 (5) and Co—N4 1.971 (5) Å] are in the same range as the equatorial Co—N distances [Co—N1 1.954 (6) and Co—N2 1.962 (6) Å]. The present axial Co—N(py) bond lengths, however, are shorter than those found in

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† Visiting Scholar from Fuyang Normal College, 236032, Anhui, China.

‡ On leave from the Department of Physics, Anna University, Madras 600 025, India.

the structure of *trans*-[Co(salen)(py)$_2$][BPh$_4$] [1.975 (3) and 1.987 (3) Å] (Shi *et al.*, 1995). Furthermore, the present equatorial Co—N distances are longer than those observed in this related Co^{III} complex [1.880 (3) and 1.896 (4) Å]. All other structural parameters have normal values. The crystal structure is stabilized by van der Waals forces.

Experimental

The complex was synthesized by reacting CoCl$_2$.6H$_2$O, pyridine and salpron (molar ratio 1:2:1) in absolute alcohol and then adding a water solution of NaBPh$_4$. The single crystals were formed by slowly diffusing petroleum into an acetone solution of the complex for a few days.

Crystal data

[Co(C$_{17}$H$_{16}$N$_2$O$_2$)(C$_5$H$_5$N)$_2$]-(C$_{24}$H$_{20}$B).C$_5$H$_5$N
$M_r = 895.76$
Orthorhombic
$P2_12_12_1$
$a = 11.934\ (2)$ Å
$b = 16.344\ (4)$ Å
$c = 24.170\ (2)$ Å
$V = 4714.3\ (15)$ Å^3
$Z = 4$
$D_x = 1.262$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8$–$25°$
$\mu = 0.412$ mm^{-1}
$T = 293\ (2)$ K
Plate
0.56 × 0.42 × 0.12 mm
Black

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4346 measured reflections
3453 independent reflections
2393 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.0351$

$\theta_{\rm max} = 22.5°$
$h = -1 \rightarrow 12$
$k = -1 \rightarrow 17$
$l = -1 \rightarrow 26$
3 standard reflections monitored every 97 reflections
intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0453$
$wR(F^2) = 0.1184$
$S = 0.932$
3452 reflections
556 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0574P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$

$\Delta\rho_{\rm max} = 0.271$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.250$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983) parameter = 0.12 (3)

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

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}/U_{\rm iso}$
Co	0.21091 (8)	0.93573 (6)	0.31863 (4)	0.0430 (3)
N1	0.1573 (5)	0.8241 (3)	0.3069 (2)	0.058 (2)
N2	0.3637 (5)	0.9107 (4)	0.2939 (2)	0.057 (2)
N3	0.1667 (5)	0.9698 (3)	0.2439 (2)	0.0452 (15)
N4	0.2467 (4)	0.9107 (3)	0.3964 (2)	0.0426 (15)
O1	0.0666 (4)	0.9695 (3)	0.3425 (2)	0.0481 (12)
O2	0.2493 (4)	1.0456 (3)	0.3327 (2)	0.0521 (13)
C1	−0.0057 (5)	0.9226 (5)	0.3689 (2)	0.044 (2)
C2	−0.0911 (6)	0.9628 (5)	0.3992 (3)	0.060 (2)
C3	−0.1698 (7)	0.9176 (7)	0.4269 (3)	0.070 (3)
C4	−0.1701 (8)	0.8352 (8)	0.4259 (3)	0.081 (3)
C5	−0.0891 (7)	0.7940 (5)	0.3954 (3)	0.066 (2)
C6	−0.0055 (6)	0.8382 (5)	0.3681 (3)	0.050 (2)
C7	0.0720 (8)	0.7949 (4)	0.3334 (3)	0.060 (2)
C8 †	0.1982 (8)	0.7690 (7)	0.2615 (5)	0.069 (4)§
C8′ ‡	0.2438 (19)	0.7662 (12)	0.2845 (10)	0.062 (8)§
C9 †	0.3214 (7)	0.7659 (6)	0.2635 (5)	0.062 (3)§
C9′ ‡	0.2863 (16)	0.7976 (17)	0.2314 (8)	0.076 (8)§
C10	0.3827 (7)	0.8427 (5)	0.2540 (3)	0.082 (3)
C11	0.4491 (6)	0.9549 (6)	0.3110 (3)	0.066 (2)
C12	0.4461 (7)	1.0268 (6)	0.3421 (3)	0.061 (2)
C13	0.5492 (8)	1.0585 (7)	0.3599 (4)	0.087 (3)
C14	0.5548 (9)	1.1309 (9)	0.3860 (5)	0.111 (4)
C15	0.4588 (10)	1.1754 (6)	0.3953 (4)	0.097 (3)
C16	0.3546 (7)	1.1459 (5)	0.3779 (3)	0.069 (2)
C17	0.3468 (7)	1.0704 (5)	0.3506 (3)	0.053 (2)
C18	0.0650 (6)	0.9529 (5)	0.2234 (3)	0.061 (2)
C19	0.0278 (7)	0.9820 (6)	0.1732 (3)	0.070 (2)
C20	0.0997 (9)	1.0307 (6)	0.1423 (4)	0.085 (3)
C21	0.2027 (7)	1.0488 (5)	0.1632 (3)	0.082 (3)
C22	0.2330 (7)	1.0188 (5)	0.2133 (3)	0.062 (2)
C23	0.3022 (6)	0.8427 (4)	0.4113 (3)	0.051 (2)
C24	0.3143 (6)	0.8217 (4)	0.4663 (3)	0.055 (2)
C25	0.2694 (6)	0.8712 (5)	0.5068 (3)	0.056 (2)
C26	0.2160 (6)	0.9410 (5)	0.4913 (3)	0.056 (2)
C27	0.2066 (6)	0.9602 (4)	0.4353 (3)	0.047 (2)
B	−0.6217 (7)	1.5047 (5)	0.3861 (3)	0.044 (2)
C28	−0.5344 (6)	1.4457 (4)	0.4183 (3)	0.043 (2)
C29	−0.5416 (7)	1.4185 (5)	0.4727 (3)	0.061 (2)
C30	−0.4596 (8)	1.3710 (6)	0.4983 (3)	0.078 (3)
C31	−0.3662 (8)	1.3485 (5)	0.4696 (4)	0.074 (3)
C32	−0.3559 (7)	1.3739 (5)	0.4173 (4)	0.072 (2)
C33	−0.4377 (7)	1.4215 (5)	0.3920 (3)	0.061 (2)
C34	−0.7362 (6)	1.5251 (5)	0.4212 (3)	0.052 (2)
C35	−0.7800 (7)	1.6041 (5)	0.4293 (3)	0.061 (2)
C36	−0.8778 (8)	1.6179 (8)	0.4603 (4)	0.090 (3)
C37	−0.9315 (8)	1.5528 (10)	0.4853 (4)	0.099 (4)
C38	−0.8939 (9)	1.4762 (9)	0.4775 (4)	0.098 (4)
C39	−0.7996 (7)	1.4626 (5)	0.4461 (3)	0.065 (2)
C40	−0.6697 (5)	1.4598 (4)	0.3297 (3)	0.044 (2)
C41	−0.7276 (7)	1.5047 (5)	0.2894 (3)	0.058 (2)
C42	−0.7731 (7)	1.4682 (6)	0.2424 (3)	0.064 (2)
C43	−0.7635 (7)	1.3858 (7)	0.2349 (4)	0.082 (3)
C44	−0.7104 (7)	1.3393 (5)	0.2743 (4)	0.068 (2)
C45	−0.6635 (6)	1.3771 (4)	0.3196 (3)	0.054 (2)
C46	−0.5511 (6)	1.5870 (4)	0.3713 (3)	0.045 (2)
C47	−0.5172 (6)	1.6393 (5)	0.4135 (4)	0.062 (2)
C48	−0.4500 (7)	1.7081 (5)	0.4040 (4)	0.073 (3)
C49	−0.4119 (7)	1.7257 (5)	0.3516 (5)	0.073 (3)
C50	−0.4416 (7)	1.6739 (6)	0.3107 (4)	0.071 (2)
C51	−0.5082 (5)	1.6075 (4)	0.3202 (3)	0.056 (2)
N5	−0.0571 (15)	0.7066 (11)	0.1772 (7)	0.228 (7)§
C52	−0.0424 (16)	0.7730 (10)	0.1384 (6)	0.177 (6)§
C53	0.0458 (17)	0.7847 (12)	0.1026 (8)	0.221 (8)§
C54	0.1261 (16)	0.7249 (10)	0.1165 (7)	0.187 (7)§
C55	0.1187 (15)	0.6692 (10)	0.1480 (6)	0.166 (6)§
C56	0.0174 (16)	0.6571 (13)	0.1862 (8)	0.225 (8)§

† Occupancy = 0.7. ‡ Occupancy = 0.3. § $U_{\rm iso}$.

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

Co—O2	1.884 (5)	N2—C10	1.490 (9)
Co—O1	1.898 (5)	O1—C1	1.319 (7)
Co—N1	1.954 (6)	O2—C17	1.306 (8)
Co—N2	1.962 (6)	C6—C7	1.436 (10)
Co—N3	1.963 (5)	C8—C9	1.471 (12)
Co—N4	1.971 (5)	C8′—C9′	1.47 (3)
N1—C7	1.294 (9)	C9—C10	1.471 (13)
N1—C8	1.501 (13)	C9′—C10	1.47 (2)
N1—C8′	1.50 (2)	C11—C12	1.394 (11)
N2—C11	1.32 (1)		

O2—Co—O1	83.6 (2)	N1—Co—N3	92.5 (2)
O2—Co—N1	174.6 (2)	N2—Co—N3	91.7 (2)
O1—Co—N1	91.0 (2)	O2—Co—N4	88.4 (2)
O2—Co—N2	91.6 (2)	O1—Co—N4	88.1 (2)
O1—Co—N2	175.1 (3)	N1—Co—N4	90.9 (2)
N1—Co—N2	93.8 (3)	N2—Co—N4	92.6 (2)
O2—Co—N3	87.8 (2)	N3—Co—N4	174.4 (2)
O1—Co—N3	87.3 (2)		

The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2. Atoms C8 and C9 were found to be disordered over two positions (C8, C8′ and C9, C9′); initially their occupancies were refined, then later fixed at 0.7 (C8 and C9) and 0.3 (C8′ and C9′). The disordered non-H atoms in the salpron ligand and the atoms of the solvent pyridine molecule were refined isotropically whereas the remaining non-H atoms were refined anisotropically. All the H atoms were generated geometrically and allowed to ride on their respective parent atoms, but not refined. The H atoms attached to C8 and C9 have occupancies of 0.7 and those at C8′ and C9′ have occupancies of 0.3. The H atoms at C10 have two positions (with 0.7 and 0.3 occupancies) corresponding to the disordered atoms C8 and C9.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1219). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(1,4-dimethylpyridinium) Bis(maleonitriledithiolato)nickelate(II)

BAO-ZHEN SHAN,[a] XIAO-MIN ZHANG,[a] XIAO-ZENG YOU,[a] HOONG-KUN FUN[b] AND KANDASAMY SIVAKUMAR[b]†

[a]*Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Centre for Advanced Studies in Science and Technology of Microstructures, Nanjing University, Nanjing 210093, People's Republic of China,* [b]*X-ray Crystallography Laboratory, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia. E-mail: hkfun@usm.my*

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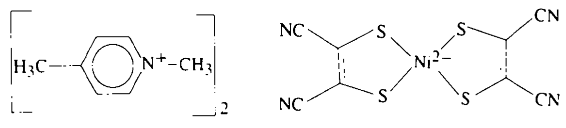
Abstract

The $[Ni(S_2C_4N_2)_2]^{2-}$ anion and $CH_3C_5H_4NCH_3^+$ cation are individually planar and their planes define a dihedral angle of 126.09 (6)°. Thick layers of anions and cations interconnected by C—H···N hydrogen bonds run parallel to the (110) planes.

Comment

1,2-Dithiolato ligands, $R_2C_2S_2^{2-}$, are capable of forming a large variety of complexes with transition metal ions in various oxidation states. The planar coordination of the metal atom to the S atoms of the ligand permits columnar ionic packing in the solid state, thereby giving rise to interesting magnetic, electrical and optical properties (Manoharan, Noordik, de Boer & Keijzers, 1981; Clemenson, 1990). The title compound, (I), the 1-methyl-4-methylpyridinium salt of the anion $[Ni(mnt)_2]^{2-}$, mnt = maleonitriledithiolate, has been synthesized to investigate its electrical and magnetic properties. The crystal structure analysis was carried out to elucidate its solid-state structural features.



(I)

A displacement ellipsoid plot of the complex with the atom-numbering scheme is shown in Fig. 1. The bond lengths and angles observed in both the anion and cation are normal. Distances in the anion agree, within experimental error, with those reported for other $[Ni(mnt)_2]^{2-}$ complexes (Mahadevan, Seshasayee, Radha & Manoharan, 1984). The Ni atom occupies an inversion centre, as

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† On leave from the Department of Physics, Anna University, Madras 600 025, India.