TEXSAN (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *TEXSAN*. Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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(Benzenethiolato-*S*)(4-*tert*-butylpyridine-*N*)bis(dimethylglyoximato-*N*,*N*′)cobalt(III) and (4-*tert*-Butylpyridine-*N*)bis(dimethylglyoximato-*N*,*N*′)(4-methoxybenzenethiolato-*S*)cobalt(III)

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Abstract

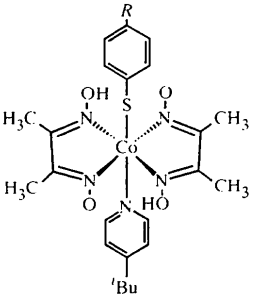
The Co—S distances in the title compounds, [Co($C_4H_7N_2O_2$)$_2$($C_9H_{13}N$)(C_6H_5S)] and [Co($C_4H_7N_2O_2$)$_2$($C_9H_{13}N$)(C_7H_7OS)], are 2.2800 (8) and 2.2885 (15) Å, respectively. The electron-donating substituent on the *para* position of the arylthiolate lengthens the Co—S bond.

Comment

A Co—S coordination is one of the possible models of coenzyme B_{12} involvement in biological methyl transfer from a tetrahydrofolate coenzyme to homosystein, which is mediated by coenzyme B_{12} (Matthews, 1984; Taylor, 1982). Model studies using cobaloxime, Co(DH)$_2$, as a coenzyme B_{12} model showed that a variety of reaction schemes are envisaged for the reaction of the cobalt complex and thiol (Schrauzer & Windgassen, 1967; Jacobsen *et al.*, 1993; Polson *et al.*, 1997). Although the crystal structures of cobaloxime derivatives, Co(DH)$_2L^1L^2$, have been widely investigated and reviewed (Pahor *et al.*, 1985; Randaccio *et al.*, 1989), only a few compounds involving sulfur ligands have been reported (L^1 and/or L^2 = S*R*; Polson *et al.*, 1997, and references therein).

As a model reaction of biological methyl transfer from methyltetrahydrofolic acid to coenzyme M, we studied the methyl transfer from the N5-methyltetrahydropteridinium ion to arylthiocobaloxime. The reaction simulated the methyl transfer from the ammonium ion to the arylthio group to give methyl aryl sulfide, and the relative reactivity of the arylthiocobaloximes decreased in the order *p*-methoxyphenylthio-, phenylthio-, *p*-chlorophenylthio- and *p*-cyanophenylthiocobaloxime (Tada *et al.*, 1998).

If the alkyl transfer starts by the initial homolysis of the Co—S bond, the reactivity must follow the bond strength and hence the bond distance of the Co—S bond. The crystal structures of [Co(DH)$_2$(4-^{t}BuPy)(PhS)], (1), and [Co(DH)$_2$(4-^{t}BuPy)(4-MeO-PhS)], (2), were investigated on this premis.



(1) *R*=H
(2) *R*=OCH$_3$

The geometries around the cobaloxime moiety [Co(DH)$_2$] are normal in both crystals. The deviation of cobalt from the best plane of the four equatorial N atoms (N1–N4) is 0.050 (1) and 0.059 (2) Å in (1) and (2), respectively, while the twisting of the two DH

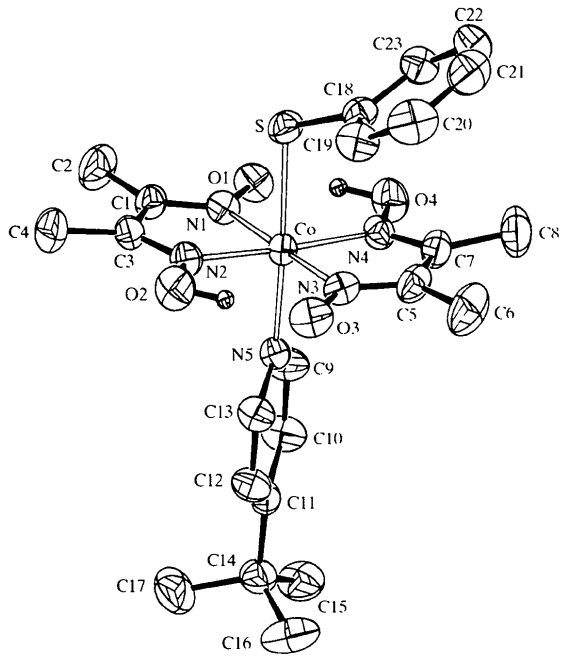


Fig. 1. The molecular structure of (1) shown with 50% probability displacement ellipsoids (*ORTEP*II; Johnson, 1976). Only the hydroxyl H atoms are shown.

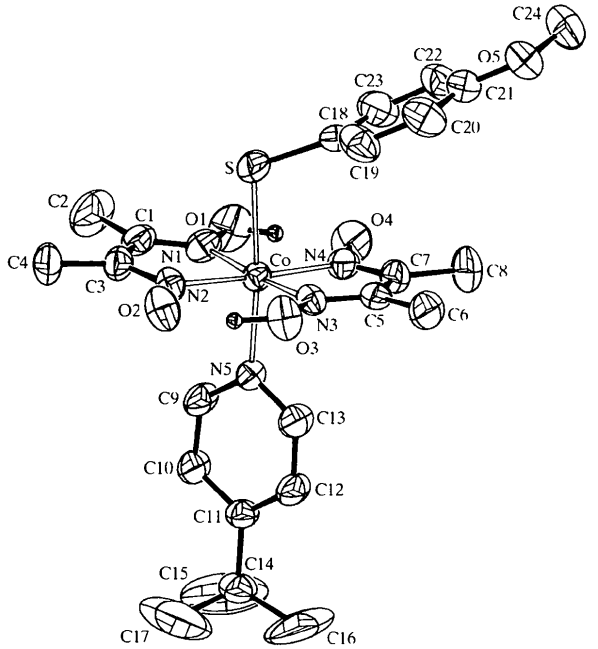


Fig. 2. The molecular structure of (2) shown with 50% probability displacement ellipsoids (*ORTEP*II; Johnson, 1976). Only the hydroxyl H atoms are shown.

planes in (1) and (2) is 9.5 (2) and 9.1 (3)°, respectively. The distances between cobalt and the axial ligands are 2.2800 (8) (Co—S) and 2.000 (2) Å (Co—N5) in (1), and 2.2885 (15) (Co—S) and 2.045 (4) Å (Co—N5) in (2). These values show clearly that the electron-donating substituent lengthens the Co—S bond. Such a trend has previously been observed in the cases of axial carbon ligands (Pahor *et al.*, 1985). The relation between the Co—S bond length and the reactivity of [Co(DH)$_2$(4-^{t}BuPy)(4-*X*-PhS)] is satisfactorily explained by assuming that the reaction starts by the initial homolysis of the Co—S bond.

Experimental

A mixture of $CoCl_2.6H_2O$ (6 mmol), dimethylglyoxime (DH_2, 12 mmol), and NaOH (12.8 mmol) was stirred under argon in 10 ml of degassed methanol (10 ml) for 10 min. 4-*tert*-Butylpyridine (6 mmol) was added and the mixture was stirred for 30 min. A solution of diaryl disulfide (5.94 mmol) in 5 ml of benzene was added and the whole was stirred at room temperature for 5 h. After filtration through a celite pad and solvent evaporation, the residue was extracted with dichloromethane (3 × 30 ml) and the extract dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by chromatography (Florisil, dichloromethane). Crystallization was carried out by diffusional mixing of hexane into a dichloromethane solution of the cobaloxime. Compound (1): m.p. 477–478 K; found: C 51.45, H 6.20, N 13.08%; calculated for $C_{23}H_{32}CoN_5O_4S$: C 51.78, H 6.05, N 13.13%. Compound (2): m.p. 482–484 K; found: C 51.22, H 6.21, N 12.39%; calculated for $C_{24}H_{34}CoN_5O_5S$: C 51.15, H 6.08, N 12.43%.

Compound (1)

Crystal data

$[Co(C_4H_7N_2O_2)_2(C_9H_{13}N)(C_6H_5S)]$	Mo $K\alpha$ radiation
M_r = 533.53	λ = 0.71073 Å
Monoclinic	Cell parameters from 25 reflections
$P2_1/a$	θ = 11.56–13.85°
a = 23.630 (6) Å	μ = 0.797 mm^{-1}
b = 10.9850 (10) Å	T = 293 (2) K
c = 9.779 (3) Å	Rod
β = 91.060 (10)°	0.20 × 0.20 × 0.10 mm
V = 2538.0 (10) Å^3	Dark green
Z = 4	
D_x = 1.396 Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer	R_{int} = 0.018
ω–2θ scans	θ_{max} = 24.99°
Absorption correction: none	h = 0 → 28
4588 measured reflections	k = 0 → 13
4469 independent reflections	l = −11 → 11
3615 reflections with $I > 2\sigma(I)$	3 standard reflections frequency: 120 min intensity decay: 0.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.090$
$S = 1.076$
4469 reflections
340 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0433P)^2 + 1.0976P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.025$
$\Delta\rho_{max} = 0.280$ e Å^{-3}
$\Delta\rho_{min} = -0.315$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (1)*

Co—N3	1.888 (2)	Co—N5	2.000 (2)
Co—N4	1.890 (2)	Co—S	2.2800 (8)
Co—N2	1.892 (2)	S—C18	1.761 (3)
Co—N1	1.893 (2)		
N3—Co—N4	81.33 (9)	N2—Co—N5	91.73 (8)
N3—Co—N2	98.59 (9)	N1—Co—N5	90.62 (8)
N4—Co—N2	175.96 (9)	N3—Co—S	93.95 (7)
N3—Co—N1	178.00 (9)	N4—Co—S	88.31 (6)
N4—Co—N1	98.92 (9)	N2—Co—S	87.66 (6)
N2—Co—N1	81.01 (9)	N1—Co—S	84.08 (7)
N3—Co—N5	91.35 (8)	N5—Co—S	174.70 (6)
N4—Co—N5	92.31 (8)	C18—S—Co	111.30 (8)

Compound (2)

Crystal data

$[Co(C_4H_7N_2O_2)_2(C_9H_{13}N)(C_7H_7OS)]$
$M_r = 563.55$
Orthorhombic
$P2_12_12_1$
$a = 12.8980$ (10) Å
$b = 18.482$ (2) Å
$c = 11.4120$ (10) Å
$V = 2720.4$ (4) Å^3
$Z = 4$
$D_x = 1.376$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.64$–$13.90°$
$\mu = 0.750$ mm^{-1}
$T = 293$ (2) K
Rod
0.20 × 0.20 × 0.15 mm
Dark green

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
2705 measured reflections
2705 independent reflections
2311 reflections with $I > 2\sigma(I)$
$\theta_{max} = 24.98°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 13$
3 standard reflections
frequency: 120 min
intensity decay: −1.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.090$
$S = 1.028$
2704 reflections
363 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0498P)^2 + 3.1260P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.045$
$\Delta\rho_{max} = 0.301$ e Å^{-3}
$\Delta\rho_{min} = -0.205$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Co—N1	1.880 (4)	Co—N5	2.045 (4)
Co—N4	1.888 (4)	Co—S	2.2885 (15)
Co—N2	1.891 (4)	S—C18	1.764 (5)
Co—N3	1.896 (4)		
N1—Co—N4	98.4 (2)	N2—Co—N5	89.86 (15)
N1—Co—N2	81.1 (2)	N3—Co—N5	92.2 (2)
N4—Co—N2	177.2 (2)	N1—Co—S	87.16 (13)
N1—Co—N3	175.6 (2)	N4—Co—S	92.42 (12)
N4—Co—N3	80.9 (2)	N2—Co—S	84.78 (12)
N2—Co—N3	99.3 (2)	N3—Co—S	88.47 (12)
N1—Co—N5	92.2 (2)	N5—Co—S	174.64 (11)
N4—Co—N5	92.9 (2)	C18—S—Co	110.2 (2)

The positions of H atoms, except those of the methyl groups, were refined, while methyl H atoms were fixed geometrically (C—H = 0.96 Å). The isotropic displacement parameters of the methyl and hydroxyl H atoms were set at 1.5 times those of the attached non-H atoms; others were set at 1.2 times. Although the *tert*-butyl group in [Co(DH)$_2$(4-^{t}BuPy)(4-MeO-PhS)], (2), is highly disordered, only one conformer was included in calculations because trials on several disorder models were not successful.

For both compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990) for (1); *MolEN* for (2). For both compounds, program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1029). Services for accessing these data are described at the back of the journal.

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