© 1998 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 71, 1805—1809 (1998)

A Sulfur-Capped Triangular Cobalt–Tributylphosphine–Aminobenzenethiolato Complex: Synthesis, Structure and Properties of $Co_3(\mu_3\text{-}S)(abt)_3(PBu^n{}_3)_3$

Zhong-Ning Chen, Bei-Sheng Kang,* Zhong-Yuan Zhou,† Wen-Jie Li,††
Ye-Xiang Tong, Zhong-Lin Lu, and Cheng-Yong Su

School of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou 510275, China
†Chengdu Institute of Organic Chemistry, Chinese Academy of Science, Chengdu 610041, China
††State Key Laboratory of Structural Chemistry and Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China

(Received December 9, 1997)

The reaction of $CoCl_2$, Habt (2-aminobenzenethiol), NaOMe and $PBu^n{}_3$ (tributylphosphine) in an equimolar ratio under anaerobic conditions, followed by the addition of an excess of Li_2S led to the triangular cluster complex $Co_3(\mu_3\text{-}S)(abt)_3(PBu^n{}_3)_3$. It crystallizes in the triclinic space group $P\bar{1}$, with $a = 13.231(2)$, $b = 14.201(2)$, $c = 18.890(2)$ Å, $\alpha = 79.970(10)°$, $\beta = 87.560(10)°$, $\gamma = 67.040(1)°$, $V = 3216.6(12)$ Å^3 and $Z = 2$. The molecule consists of three "Co(abt)($PBu^n{}_3$)" units with the Co_3 plane capped by the bridging μ_3-S atom to form an approximately equilateral triangle with an average Co–Co distance of 2.709 Å. The cobalt atoms located in distorted trigonal-bipyramidal environments are further bridged by μ_2-S atoms from the three abt ligands and terminally coordinated by N and P donors. The cyclic voltammogram showed three quasi-reversible redox processes with $E_{1/2} = 0.79$, -0.07, and -0.81 V, vs. SCE. The variable-temperature magnetic susceptibility measurements showed an antiferromagnetic exchange interaction within the triangular spin cluster.

Increasing interest has recently been focused on the syntheses, reactivity, and characterization of metal-thiolato clusters with phosphine ligands, chiefly owing to their potential applications as industrial catalysts$^{1)}$ and drugs$^{2)}$ as well as molecular materials$^{3,4)}$ possessing peculiar optical, electrical or magnetic properties. The reaction of transition metal ions with 1,2-bidentate thiolato ligands in the presence of tertiary phosphines has been found to be an efficacious methodology for the assembly of such clusters$^{5,6)}$ and a series of asymmetric tri- and tetranuclear cobalt clusters$^{4,7—9)}$ with cyclic metal skeletons has been isolated. It is noteworthy that the phosphine donors, which are invariably located at the square-based pyramidal or trigonal bipyramidal apices of the cobalt polyhedra, play a key role in the formation and stabilization of the cyclic molecular assembly.$^{4,6—9)}$ Obviously, the mixed S, P ligation results in a so-called synergistic coordination effect.$^{10)}$

We have engaged in the systematic study of the coordination chemistry of phosphine-participated homo-$^{4—12)}$ and heterometallic$^{13,14)}$ complexes with spin clusters, and have employed sulfur-containing chelating ligands such as dithiolate ($S\frown S$), aminothiolate ($N\frown S$), and hydroxythiolate ($O\frown S$). In order to extend this work, sulfide is introduced into the metal–thiolate–phosphine system and the μ_3-S capped triangular complex $Co_3(\mu_3\text{-}S)(abt)_3(PBu^n{}_3)_3$ was isolated. Herein we report its structure together with the magnetic behavior. To our knowledge, there are few examples of phosphine-containing cobalt clusters$^{9)}$ with thiolato as well as sulfide bridging ligands.

Experimental

All operations were carried out under a dinitrogen atmosphere with Schlenk-type apparatus. 2-Aminobenzenethiol (o-$HSC_6H_4NH_2$ = Habt), tributylphosphine ($PBu^n{}_3$), and anhydrous cobalt(II) chloride were used as received. Absolute ethanol was flushed with pure dinitrogen for 5 min before use. Sodium methoxide was prepared by dissolving sodium metal in dry methanol and then evaporating the solvent, and was dried under reduced pressure.

Preparation. To the absolute ethanol solution (30 ml) containing $CoCl_2$ (1.0 mmol, 0.13 g) and NaOMe (2.0 mmol, 0.11 g) were added via syringes first 0.25 ml (1.0 mmol) of $PBu^n{}_3$, and then 0.10 ml (1.0 mmol) of Habt with stirring. The solution color turned deep orange after 10 min; then to it a methanol solution (10 ml) of Li_2S (1.0 mmol) was added. The reaction mixture then turned to a deeper color of dark brown. It was stirred for half an hour more before filtration. The black filtrate was allowed to stand at 4 °C for several days to give well-shaped brownish-black crystals with yield of 38%. Found: C, 54.41; H, 8.25; N, 3.38; P, 7.68; S, 10.59; Co, 14.97%. Calcd for $C_{54}H_{99}N_3P_3S_4Co_3$: C, 54.53; H, 8.31; N, 3.53; P, 7.83; S, 10.77; Co, 15.03%. IR (KBr) 3481 (w), 3275 (w), 3200 (w), 3053 (w), 2954 (s), 2929 (w), 2870 (m), 1574 (w), 1463 (s), 1439 (s), 1296 (m), 1280 (m), 1092 (m), 903 (m), 752 (m), 719 (m), 622 (w), 565 (w), 492 (w), 446 (m), 430 (m), 401 (m), and 366 (m) cm^{-1}. The Far-IR spectrum showed a sharp band at 446 cm^{-1} attributable to the Co-(μ_3-S) vibration.$^{15)}$

X-Ray Crystallography. A single crystal with suitable dimensions was mounted on a glass fiber. Data collection was performed on a Siemens P4 diffractometer by $\overline{\omega}$ scan technique using graphite-monochromated Mo*Kα* radiation (λ = 0.71073 Å). The crystal data, data collection and refinement parameters are summarized in Table 1.

The coordinates of the metal atoms were determined by direct methods and the remaining non-hydrogen atoms were located from successive Fourier difference syntheses. The structure was refined by full-matrix least-squares techniques with anisotropic thermal parameters for all the non-hydrogen atoms. The positions of the hydrogen atoms were isotropically added to the structural factor calculations but not refined. All calculations were performed on an IBM PC/486 computer with the Siemens SHELXTL-P4/PC program package.[16] Atomic coordinates and isotropic thermal parameters are presented in Table 2. The $F_o - F_c$ table has been deposited as Document No. 71040 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Physical Measurements. The IR spectrum was obtained from a Perkin–Elmer 577 spectrophotometer. Cyclic voltammetric measurements were performed on an HDV-7B potentiostat with DCD-3 frequency generator, equipped with a LZ32-204 X–Y recorder in a three-electrode cell with platinum working and auxiliary electrodes and a saturated calomel electrode (SCE) as reference. The supporting electrolyte was $Bu^n{}_4NClO_4$ (0.1 mol dm^{-3}) and scan rate was 100 mV s^{-1}. Variable-temperature magnetic susceptibilities in the temperature range 4—300 K were measured on a model CF-1 superconducting extracting sample magnetometer at a magnetic field of 5.0 T with the powdered samples kept in capsules for weighing.

Results and Discussion

As a simple aromatic thiolato ligand containing S and N

Table 1. Summary of Crystal Data, Data Collection, and Refinement Parameters of $Co_3(\mu_3\text{-}S)(abt)_3(PBu^n{}_3)_3$

Formula	$C_{54}H_{99}N_3P_3S_4Co_3$
MW	1188.3
Space group	$P\bar{1}$ (No. 2)
T/°C	21
λ (Mo *Kα*)/Å	0.71073
a/Å	13.231(2)
b/Å	14.201(2)
c/Å	18.890(2)
α/°	79.970(10)
β/°	87.560(10)
γ/°	67.040(10)
V/Å^3	3216.6(12)
Z	2
ρ_{calcd}/g cm^{-3}	1.227
μ(Mo *Kα*)/cm^{-1}	10.03
2θ range/°	3.0—50.0
h, k, l Ranges	−1—14, −15—15, −21—21
Independent reflections	10028
Observed reflections [$F > 4.0\sigma(F)$]	5985
$R^{a)}(F_o)$	0.0563
$R_w{}^{b)}(F_o)$	0.0650
Goodness of fit	1.84
Largest and mean Δ/σ	0.009, 0.003
Residual extrema/e Å^{-3}	+0.57 to −0.50

a) $R = \sum||F_o| - |F_c||/\sum|F_o|$. b) $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w^{-1} = \sigma^2(F) + 0.0005F^2$.

Table 2. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (U_{eq}) for $Co_3(\mu_3\text{-}S)(abt)_3(PBu^n{}_3)_3$

Atom	x	y	z	U_{eq}
Co(1)	0.3973(1)	0.0793(1)	0.7856(1)	0.054(1)
Co(2)	0.3008(1)	0.1514(1)	0.6541(1)	0.056(1)
Co(3)	0.2081(1)	0.2508(1)	0.7673(1)	0.056(1)
S(1)	0.3060(1)	0.1626(1)	0.8719(1)	0.060(1)
S(2)	0.4548(1)	0.0153(1)	0.6810(1)	0.063(1)
S(3)	0.1392(1)	0.2920(1)	0.6560(1)	0.063(1)
S(4)	0.3685(1)	0.2321(1)	0.7194(1)	0.059(1)
N(1)	0.3429(2)	−0.0233(2)	0.8235(2)	0.066(1)
N(2)	0.2353(2)	0.0609(2)	0.6479(2)	0.070(1)
N(3)	0.0911(2)	0.2083(2)	0.7923(2)	0.065(1)
C(1)	0.2529(2)	0.0728(2)	0.9130(2)	0.059(1)
C(2)	0.1854	0.0863	0.9722	0.075(1)
C(3)	0.1396	0.0140	0.9981	0.095(1)
C(4)	0.1614	−0.0719	0.9647	0.102(1)
C(5)	0.2290	−0.0854	0.9054	0.094(1)
C(6)	0.2747	−0.0130	0.8795	0.068(1)
C(7)	0.4059(2)	−0.0799(2)	0.6739(2)	0.074(1)
C(8)	0.4075	−0.1861	0.6865	0.086(1)
C(9)	0.4225	−0.2575	0.6850	0.122(1)
C(10)	0.3099	−0.2227	0.6710	0.133(1)
C(11)	0.2454	−0.1166	0.6584	0.106(1)
C(12)	0.2934	−0.0452	0.6599	0.072(1)
C(13)	0.0208(2)	0.2077(2)	0.7435(2)	0.063(1)
C(14)	−0.0612	0.1690	0.7590	0.82(1)
C(15)	−0.1302	0.1725	0.7040	0.106(1)
C(16)	−0.1173	0.2145	0.6334	0.101(1)
C(17)	−0.0353	0.2532	0.6179	0.084(1)
C(18)	0.0332(2)	0.2480(2)	0.6722(2)	0.062(1)
P(1)	0.5604(1)	0.0258(1)	0.8374(1)	0.060(1)
C(19)	0.5802(2)	−0.0865(2)	0.9077(2)	0.074(1)
C(20)	0.6021(2)	−0.1860(2)	0.8792(2)	0.098(1)
C(21)	0.6003(2)	−0.2734(2)	0.9334(2)	0.168(1)
C(22)	0.6283(2)	−0.3698(2)	0.9049(2)	0.291(1)
C(23)	0.6777(2)	−0.0175(2)	0.7807(2)	0.070(1)
C(24)	0.7921(2)	−0.0613	0.8180(2)	0.089(1)
C(25)	0.8846(2)	−0.1156(2)	0.7706(2)	0.120(1)
C(26)	0.9957(2)	−0.1525(2)	0.8050(2)	0.214(1)
C(27)	0.5855(2)	0.1142(2)	0.8855(2)	0.073(1)
C(28)	0.5972(2)	0.2077(2)	0.8385(2)	0.089(1)
C(29)	0.6217(2)	0.2772(2)	0.8792(2)	0.122(1)
C(30)	0.6403(2)	0.3650(2)	0.8339(2)	0.181(1)
P(2)	0.3422(2)	0.2009(1)	0.5429(1)	0.065(1)
C(31)	0.3361(2)	0.1119(2)	0.4870(2)	0.079(1)
C(32)	0.2176(2)	0.1260(2)	0.4689(2)	0.098(1)
C(33)	0.2103(2)	0.0336(2)	0.4455(2)	0.139(1)
C(34)	0.0915(2)	0.0474(2)	0.4346(2)	0.215(1)
C(33)	0.2103(2)	0.0336(2)	0.4455(2)	0.139(1)
C(34)	0.0915(2)	0.0474(2)	0.4346(2)	0.215(1)
C(35)	0.2518(2)	0.3292(2)	0.4954(2)	0.071(1)
C(36)	0.2786(2)	0.3586(2)	0.4164(2)	0.090(1)
C(37)	0.1967(2)	0.4617(2)	0.3826(2)	0.105(1)
C(38)	0.2186(2)	0.4925(2)	0.3048(2)	0.147(1)
C(39)	0.4852(2)	0.1935(2)	0.5299(2)	0.082(1)
C(40)	0.5474(2)	0.2450(2)	0.5704(2)	0.241(1)
C(41)	0.4897(2)	0.3446(2)	0.5700(2)	0.301(1)
C(42)	0.5766(2)	0.3740(2)	0.6020(2)	0.405(1)
P(3)	0.1620(2)	0.4065(1)	0.7934(1)	0.078(1)
C(43)	0.1125(2)	0.5138(2)	0.7182(2)	0.100(1)
C(44)	0.1977(2)	0.5205(2)	0.6635(2)	0.106(1)
C(45)	0.1371(2)	0.6185(2)	0.6036(2)	0.258(1)
C(46)	0.2274(2)	0.6103(2)	0.5548(2)	0.277(1)
C(47)	0.2701(2)	0.4271(2)	0.8357(2)	0.088(1)
C(48)	0.2450(2)	0.5336(2)	0.8569(2)	0.133(1)
C(49)	0.3449(2)	0.5442(2)	0.8839(2)	0.226(1)
C(50)	0.3261(2)	0.6394(2)	0.9035(2)	0.374(1)
C(51)	0.0397(2)	0.4447(2)	0.8490(2)	0.123(1)
C(52)	0.0568(2)	0.3793(2)	0.9202(2)	0.151(1)
C(53)	−0.0387(2)	0.3793(2)	0.9721(2)	0.232(1)
C(54)	−0.1165(2)	0.3631(2)	0.9313(2)	0.400(1)

donors, 2-aminobenzenethiol (Habt) can usually chelate as well as bridge various metal ions in the form of a monoanion abt (o-$NH_2C_6H_4S^-$). When the reaction of Habt and $CoCl_2$ was carried out in the presence of PR_3, various products were isolated depending on the molar ratio of the reactants as well as on whether or not strict anaerobic conditions were followed. The reaction mixture of $CoCl_2$, $PBu^n{}_3$, Habt and NaOMe in the molar ratio of 1 : 2 : 2 : 2 gave first probably the unstable mononuclear species $Co(abt)_2(PBu^n{}_3)_2$ under anaerobic reaction conditions, whereas the cation $[Co(abt)_2(PBu^n{}_3)_2]^+$ was formed[17] with the oxidation of Co(II) into Co(III) when air leaked into the reaction system, and the salt $[Co(abt)_2(PBu^n{}_3)_2](BF_4)$ was isolated.[17] If the reaction is performed with the reactants in a molar ratio of 1 : 1 : 1 : 2, followed by the addition of an excess amount of Li_2S, the trinuclear cluster complex $Co_3(\mu_3\text{-}S)(abt)_3(PBu^n{}_3)_3$ was obtained. This triangular complex could be visualized as being constructed from three of the phosphine-thiolato units "$Co(abt)(PR_3)$", so called building blocks,[4—6] united by a μ_3-S bridge. Instead of S^{2-}, if some other anion such as $N_3{}^-$ or OCN^- was employed as the bridging group, no stable complex could be isolated, thus indicating that the sulfide bridge stabilizes the phosphine-thiolato structural units "$Co(abt)(PR_3)$" while constructing cluster complexes. This phenomenon certifies once again that the synergistic effect[10] of mixed S, P ligation favors the formation of clusters.

A drawing of complex (**1**) with atomic numbering scheme is given in Fig. 1. Selected atomic distances and bond angles are compiled in Table 3. The molecule with the Co_3 plane capped by the μ_3-S bridging atom forms an approximately equilateral triangle with average Co–Co distance of 2.709 Å. The μ_3-S atom is displaced away from the plane by 1.559 Å. The Co–Co distance is slightly shorter than those found in μ_3-S bridged complexes $(Et_4N)_2[Co_3(\mu_3\text{-}S)\{1,2\text{-}(SCH_2)_2C_6H_4\}_3]\cdot MeCN$ (average 2.806 Å)[18a] and $(Me_4N)_2[Co(\mu_3\text{-}S)\{1,2\text{-}(SCH_2)_2C_6H_4\}_3]\cdot 2MeOH$ (average 2.780 Å)[18b] without the phosphine ligands, but longer than those (average 2.36—2.57 Å) in the isosceles triangular cluster $Co_3(S^\frown S)_3(PR_3)_3$[7] ($S^\frown S = 1,2$-benzenedithiolate) and in the asymmetrical complex $Co_3(mp)_2(Hmp)_2(PR_3)_3$[4] ($H_2mp$ = 2-mercaptophenol) without the involvement of μ_3-S bridge. However, the corresponding distance is significantly shorter than those (average 3.046 Å) in the cation $[Co_3(\mu_3\text{-}S)_2(\mu\text{-}SH)(\mu\text{-}PEt_2)(PHEt_2)_6]^{2+}$, [19] with doubly μ_3-S bridges.

Table 3. Selected Atomic Distances (Å) and Bond Angles (°) of $Co_3(\mu_3\text{-}S)(abt)_3(PBu^n{}_3)_3$

Co(1)–Co(2)	2.688(1)	Co(1)–S(4)	2.207(2)
Co(2)–Co(3)	2.729(1)	Co(2)–S(4)	2.213(3)
Co(1)–Co(3)	2.709(1)	Co(3)–S(4)	2.208(2)
Co(1)–S(1)	2.216(2)	Co(1)–S(2)	2.294(2)
Co(2)–S(2)	2.214(2)	Co(2)–S(3)	2.271(2)
Co(3)–S(3)	2.217(2)	Co(3)–S(1)	2.289(2)
Co(1)–N(1)	1.888(3)	Co(1)–P(1)	2.197(2)
Co(2)–N(2)	1.864(4)	Co(2)–P(2)	2.203(2)
Co(3)–N(3)	1.885(3)	Co(3)–P(3)	2.192(2)
Co(1)–Co(2)–Co(3)	60.0(1)	S(1)–Co(1)–S(2)	166.7(1)
Co(1)–Co(3)–Co(2)	59.2(1)	S(2)–Co(2)–S(3)	166.0(1)
Co(2)–Co(1)–Co(3)	60.7(1)	S(1)–Co(3)–S(3)	163.3(1)
S(4)–Co(1)–N(1)	148.7(1)	S(4)–Co(1)–P(1)	106.2(1)
S(4)–Co(2)–N(2)	150.2(1)	S(4)–Co(2)–P(2)	104.3(1)
S(4)–Co(3)–N(3)	153.3(1)	S(4)–Co(3)–P(3)	98.8(1)
N(1)–Co(1)–P(1)	104.9(1)	Co(1)–S(1)–Co(3)	73.9(1)
N(2)–Co(2)–P(2)	105.2(1)	Co(1)–S(2)–Co(2)	73.2(1)
N(3)–Co(3)–P(3)	107.8(1)	Co(2)–S(3)–Co(3)	74.9(1)
Co(1)–S(1)–C(1)	98.8(1)	Co(3)–S(1)–C(1)	108.9(1)
Co(2)–S(2)–C(7)	99.0(1)	Co(1)–S(2)–C(7)	110.0(1)
Co(3)–S(3)–C(18)	98.1(2)	Co(2)–S(3)–C(18)	109.3(1)
Co(1)–S(4)–Co(2)	74.9(1)	Co(1)–N(1)–C(6)	122.2(2)
Co(2)–S(4)–Co(3)	76.3(1)	Co(2)–N(2)–C(12)	122.5(2)
Co(1)–S(4)–Co(3)	75.7(1)	Co(3)–N(3)–C(13)	122.9(3)

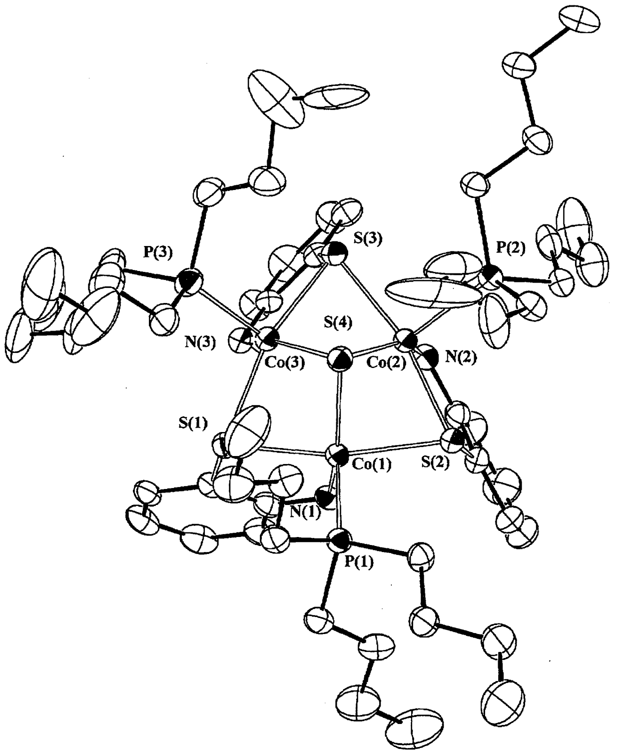

Fig. 1. Thermal ellipsoid plot (50%) showing the atom-labelling scheme for the complex $Co_3(\mu_3\text{-}S)(abt)_3(PBu^n{}_3)_3$.

The Co atoms in complex (**1**) are further bridged by three μ_2-S(1—3) atoms from the three abt ligands and terminally coordinated by the atoms N(1—3) and P(1—3). In this way, each abt ligand furnishes one bridging S and one terminal N atoms to form a five-membered chelate ring $\overline{\text{CoNCCS}}$. The distances of Co–S inside the five-membered chelate ring (average 2.216 Å) are obviously shorter than those outside (average 2.285 Å), as is often observed in the homonuclear metal clusters of mixed phosphine and 1,2-dithiolate[7,9,11,12] or 2-mercaptophenolate.[4,5,8] Accordingly, on the basis of the idea of combination of structural units in the construction of cluster complexes proposed previously,[4,6,10] the triangular cobalt molecule can be envisaged as the assembly of three mononuclear building blocks "Co(abt)(PBu$^n{}_3$)" by three μ_2-S and one μ_3-S bridges. The average Co–(μ_3-S) distance (2.209 Å) in this complex is slightly longer than that in $Co_3S(CO)_6(PPh_3)(S_2COMe)$ (average 2.160 Å)[20] with two carbonyl groups per Co atom, but is obviously shorter than those in $[Co_3S(1,2\text{-}(SCH_2)_2C_6H_4)_3]^{2-}$ (average 2.275 Å)[18] and $[Co_3(\mu_3\text{-}S)_2(\mu\text{-}SH)(\mu\text{-}PEt_2)(PHEt_2)_6](ClO_4)_2$ (average 2.292 Å).[19] The planes of P_3 and N_3 are situated above (average 1.160 Å), and below (1.786 Å) the Co_3 plane, respectively, and are virtually parallel to it with the dihedral angles $< 2.5°$, while the planes S_3 and Co_3 are coplanar. The largest deviation of atom S(3) from the plane defined by the six atoms is only 0.052 Å. Such arrangements afford a C_3 symmetry to the molecule with the axis passing through the μ_3-S(4) atom and perpendicular to the planes defined by atoms Co_3, S_3, N_3, and P_3. The geometry of the cobalt atoms is better described as a trigonal bipyramid, which places the μ_2-S atom in the axial site for each cobalt center. The cobalt atoms (1—3) deviate by 0.054, 0.055, and 0.039 Å, respectively, from the trigonal planes of P(n)N(n)S(4) ($n = 1,2,3$), although the trigonal axes show much distortion from linearity with the axial angles S_m–Co–S_n ($m \neq 1,2,3$) being 166.7—163.3°.

The average chelate angles Co–N–C and Co–S–C within a ring are 122.5° and 98.7°, respectively, showing similar trends as the ligand 2-mercaptophenol[10] in complexes of which the angle M–S–C is always smaller than M–O–C by nearly 20°. The neutral nature of the complex necessitates a formal oxidation of +5 for the three cobalt atoms.

The cyclic voltammogram of $Co_3(\mu_3\text{-}S)(abt)_3(PBu^n{}_3)_3$ is depicted in Fig. 2. Three redox processes are observed with $E_{1/2} = 0.79$, -0.07, and -0.81 V vs. SCE, for the redox couples 0/+1, −1/0, and −2/−1, respectively. For each redox couple, the peak separation of about 100 mV and the almost equivalent peak current values ($I_a/I_c \approx 1$) suggest that quasireversible one-electron redox processes are involved. Thus $Co_3(\mu_3\text{-}S)(abt)_3(PBu^n{}_3)_3$ can be considered as a member of the four-component electron-transfer series according to the scheme below:

$$\begin{tikzcd}
{[Co_3(S)(abt)_3(PBu^n{}_3)_3]^+} \arrow[r, shift left, "+e"] & {[Co_3(S)(abt)_3(PBu^n{}_3)_3]^0} \arrow[l, shift left, "-e"] \arrow[d, shift left, "+e"] \\
{[Co_3(S)(abt)_3(PBu^n{}_3)_3]^{-2}} \arrow[r, shift left, "-e"] & {[Co_3(S)(abt)_3(PBu^n{}_3)_3]^-} \arrow[l, shift left, "+e"] \arrow[u, shift left, "-e"]
\end{tikzcd}$$

(1)

The measured temperature dependence of the magnetic moment per Co_3 unit of the title complex in the form of μ_{eff} vs. T is shown in Fig. 3. The observed effective magnetic moment decreases on decreasing temperature from a value of 3.60 μ_B at 300 K to 1.62 μ_B at 4 K, indicating an antiferromagnetic exchange interaction. Although the total metal oxidation state of the complex is +5/3 per molecule, it may be described as a mixed-valence species with the assumption of 2Co(II) ($S = 1/2$)+Co(I) ($S = 1$) when interpreting its magnetic exchange interactions. As a basis for the interpretation of the magnetic data, we started from the isotropic Heisenberg Hamiltonian for three paramagnetic centers:[21]

$$\hat{H} = -2J_1(S_1 \cdot S_2 + S_2 \cdot S_3) - 2J_2 S_1 \cdot S_3,$$

with J_i ($i = 1$ or 2) as the exchange coupling constant. By means of the van Vleck equation, a theoretical expression for the temperature dependence of the molar susceptibility can be obtained. The best parameters obtained from least-square fits to the experimental data are $g = 2.08$ and $J_1 = -21.0$ and $J_2 = -39.3$ cm^{-1} with an agreement factor $R = \Sigma(\mu_{obsd} - \mu_{calcd})^2/\Sigma(\mu_{obsd})^2$ of 4×10^{-4}. The result of the fitting is shown as the solid curve in Fig. 3. Intramolecular

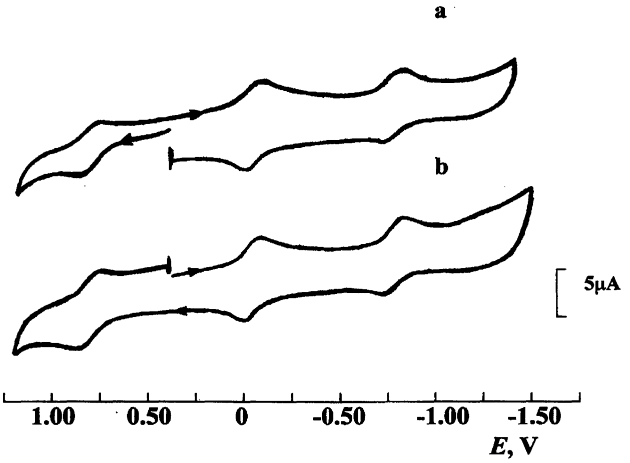

Fig. 2. Cyclic voltammograms of the complex $Co_3(\mu_3\text{-}S)(abt)_3(PBu^n{}_3)_3$ (10^{-4} mol dm^{-3}) in DMF/$(Bu^n{}_4N)ClO_4$ (10^{-1} mol dm^{-3}) at a Pt electrode with a scan rate of 0.1 V s^{-1} (potential in volts vs. SCE.) a) Begin with oxidation. b) Begin with reduction.

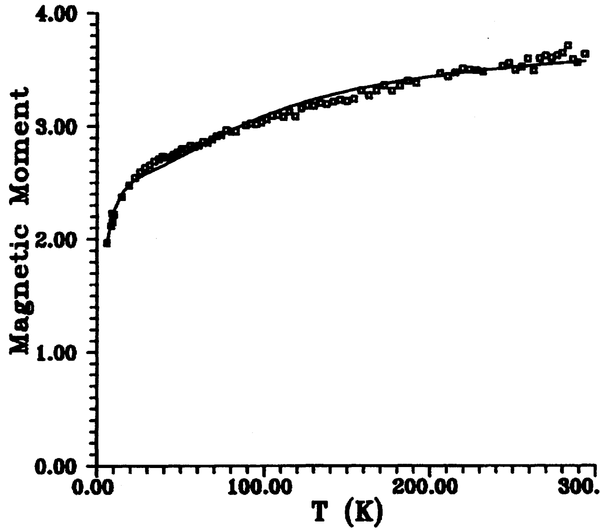

Fig. 3. Plot of the temperature dependence of the magnetic moment μ_{eff} (μ_B) for $Co_3(\mu_3\text{-}S)(abt)_3$ $(PBu^n{}_3)_3$. The solid line represents the best calculated values.

antiferromagnetic interaction is shown to present between the cobalt centers.

This work was supported by NNSF of China, by the State Key Laboratory of Structure Chemistry, and by the Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

References

1) a) K. J. Cavell, D. G. Hay, A. F. Masters, and G. A. Williams, *Aust. J. Chem.*, **38**, 369 (1985); b) K. J. Cavell, D. G. Hay, A. F. Masters, and G. A. Williams, *Aust. J. Chem.*, **37**, 273 (1984).

2) M. C. Gimeno, P. C. Jones, A. Laguna, M. Laguna, and R. Terroba, *Inorg. Chem.*, **33**, 3932 (1994).

3) a) J. M. Forward, D. Bohmann, J. P. Fackler, Jr., and R. J. Staples, *Inorg. Chem.*, **34**, 6330 (1995); b) Z. Assefa, B. G. McBurnrtt, R. J. Staples, J. P. Fackler, Jr., B. Assmann, K. Angermater, and H. Schmiddbaur, *Inorg. Chem.*, **34**, 75 (1995).

4) B. S. Kang, Y. J. Xu, X. L. Xie, C. N. Chen, Q. T. Liu, H. Q. Liu, and J. X. Lu, *Inorg. Chem.*, **33**, 3770 (1994).

5) Z. N. Chen, B. S. Kang, Z. Lin, B. M. Wu, Z. Y. Zhou, T. C. W. Mak, C. N. Chen, and Q. T. Liu, *J. Chem. Soc., Dalton Trans.*, **1996**, 177.

6) B. S. Kang, M. C. Hong, T. B. Wen, H. Q. Liu, and J. X. Lu, *J. Cluster Sci.*, **6**, 379 (1995).

7) B. S. Kang, J. H. Peng, M. C. Hong, D. X. Wu, X. T. Chen, L. H. Weng, X. J. Lei, and H. Q. Liu, *J. Chem. Soc., Dalton Trans.*, **1991**, 2897.

8) Y. J. Xu, B. S. Kang, X. T. Chen, Y. B. Cai, Y. H. Hu, and J. X. Lu, *J. Cluster Sci.*, **3**, 167 (1992).

9) F. L. Jiang, Z. Y. Huang, D. X. Wu, B. S. Kang, M. C. Hong, and H. Q. Liu, *Inorg. Chem.*, **32**, 4971 (1993).

10) B. S. Kang, Z. N. Chen, Z. Y. Zhou, H. Q. Liu, H. R. Gao, B. M. Wu, T. C. W. Mak, Y. B. Cai, Y. J. Xu, and Z. T. Xu, *J. Cluster Sci.*, **7**, 317 (1996).

11) a) F. L. Jiang, Z. Y. Huang, M. C. Hong, R. Cao, D. X. Wu, and H. Q. Liu, *Chin. J. Chem.*, **12**, 481 (1994); b) F. L. Jiang, X. L. Xie, M. C. Hong, B. S. Kang, R. Cao, D. X. Wu, and H. Q. Liu, *J. Chem. Soc., Dalton Trans.*, **1995**, 1447.

12) B. S. Kang, Y. J. Xu, D. X. Wu, J. H. Peng, M. C. Hong, L. H. Weng, X. T. Chen, and H. Q. Liu, *Sci. China B*, **23**, 132 (1993).

13) Z. N. Chen, W. J. Li, B. S. Kang, M. C. Hong, Z. Y. Zhou, T. C. W. Mak, Z. Lin, X. M. Chen, and H. Q. Liu, *Inorg. Chem.*, **36**, 208 (1997).

14) Z. N. Chen, W. J. Li, B. S. Kang, H. X. Zhang, Z. Y. Zhou, T. C. W. Mak, Y. B. Cai, M. C. Hong, and H. Q. Liu, *J. Chin. Chem. Soc.*, in press (1998).

15) Y. Yang, Q. T. Liu, and D. X. Wu, *Inorg. Chim. Acta*, **208**, 85 (1993).

16) G. M. Sheldrick, "SHELXTL PC," Siemens Analytical X-Ray Instruments, Inc., Madison, Wisconsin, USA (1990); G. M. Sheldrick, in "Computational Crystallogrphy,"ed by D. Sayre, Oxford University Press, New York (1982).

17) Z. N. Chen, unpublished work.

18) a) G. Henkel, W. Tremel, and B. Krebs, *Angew. Chem., Int. Ed. Engl.*, **22**, 318 (1983); b) K. S. Hogen, G. Christou, and R. H. Holm, *Inorg. Chem.*, **22**, 309 (1983).

19) C. A. Ghilardi, S. Midollini, A. Orlandini, and G. Scanacci, *J. Chem. Soc., Dalton Trans.*, **1992**, 2909.

20) R. D. Gillard and H. U. Hummel, *Transition Met. Chem.*, **10**, 348 (1985).

21) R. D. Cannon and R. P. White, *Prog. Inorg. Chem.*, **36**, 195 (1988).