Synthesis and *X*-Ray Structure of an Asymmetrical Dicobalt(II) Complex $Co_2(dppe)(\mu\text{-}SPh)_3SPh$ (dppe = $Ph_2PCH_2CH_2PPh_2$)

Guowei Wei, Hanqin Liu,* Zhiying Huang, Liangren Huang, and Beisheng Kang

Fuzhou Laboratory of Structural Chemistry and Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

An asymmetrical dinuclear cobalt complex $Co_2(dppe)(\mu\text{-}SPh)_3SPh$ (dppe = $Ph_2PCH_2CH_2PPh_2$) has been prepared and characterized by *X*-ray diffraction showing the entirely different geometrical environments of the two cobalt(II) atoms.

Despite the fact that cobalt compounds with bidentate phosphine ligands are common,[1] there has been no report of a cobalt complex with both bidentate phosphino and monodentate thiolate ligands. Owing to their exceptional structural features, we explored the reaction of $CoCl_2$, NaSPh, and diphenylphosphino ligands (dppm, dppe, and dppp)† and the

---

† *Abbreviations used:* dppm = $Ph_2PCH_2PPh_2$, dppe = $Ph_2PCH_2CH_2PPh_2$ [1,2-bis(diphenylphosphino)ethane], dppp = $Ph_2PCH_2CH_2CH_2PPh_2$, subscript b for bridge.

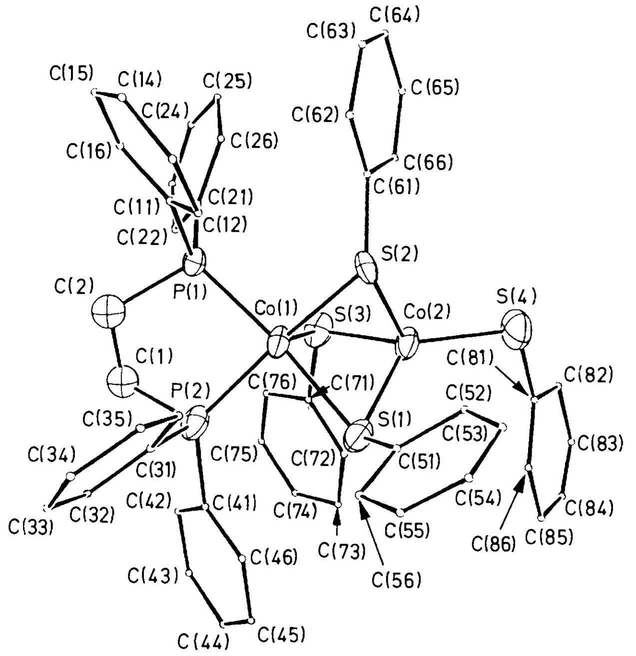

Figure 1. Structure of the dinuclear molecule $Co_2(dppe)(SPh)_4$. Selected atomic distances (Å): Co(1)–Co(2) 2.632(2), Co(1)–S(1) 2.352(3), Co(1)–S(2) 2.273(3), Co(1)–S(3) 2.376(3), Co(1)–P(1) 2.226(3), Co(1)–P(2) 2.194(3), Co(2)–S(1) 2.298(3), Co(2)–S(2) 2.310(3), Co(2)–S(3) 2.263(3), Co(2)–S(4) 2.215(4); and bond angles (°): P(1)–Co(1)–P(2) 86.7(1), Co(1)–P(1)–C(2) 107.3(4), P(1)–C(2)–C(1) 110.5(7), C(2)–C(1)–P(2) 107.6(7), C(1)–P(2)–Co(1) 107.5(4), S(1)–Co(1)–S(2) 85.0(1), S(1)–Co(1)–S(3) 91.0(1), S(2)–Co(1)–S(3) 92.7(1), S(1)–Co(2)–S(2) 85.4(1), S(1)–Co(2)–S(3) 95.4(1), S(2)–Co(2)–S(3) 94.7(1), Co(1)–Co(2)–S(4) 169.0(2).

formation of the various molecular structures. Herein, we report the preparation and crystal structure of an asymmetrical complex $Co_2(dppe)(\mu\text{-}SPh)_3SPh$.

A mixture of NaSPh (0.26 g, 2 mmol) and elemental selenium (0.08 g, 1 mmol) in dimethylformamide (DMF) (20 ml) was stirred at room temperature for 0.5 h and produced a crimson solution. The complex $Co(dppe)Cl_2$ (0.53 g, 1 mmol) was added to the solution to give a crimson black mixture after stirring for another 0.5 h. The solution was then reduced to a quarter of its volume by low pressure evaporation at 45 °C and added to 40 ml of acetone. The brown precipitate was removed by filtration. Black, plate-like crystals (0.68 g, 71%) suitable for *X*-ray analysis were obtained after allowing the filtrate to stand at 0 °C for a week. The by-product $dppeSe_2$ [equation (1)] was characterized by atomic and ^{31}P NMR spectra.[2] Elemental analyses of the compound were satisfactory. The IR spectroscopic results were (KBr) 526.6vs, 513.1vs, 387.7m, 366.5s, and 204.5m cm^{-1}, recorded on a Digilab-20E/D spectrophotometer. A black plate-like crystal of dimensions 0.2 × 0.2 × 0.04 mm was used for the *X*-ray work.‡

$$4NaSPh + 2Se + 2Co(dppe)Cl_2 \rightarrow Co_2(dppe)(SPh)_4 + dppeSe_2(SPh)_4 + dppeSe_2 + 4NaCl \downarrow \quad (1)$$

The structure of the dicobalt compound $Co_2(dppe)(\mu\text{-}SPh)_3SPh$ is depicted in Figure 1, along with important atomic distances and bond angles. The molecule of the dinuclear compound is asymmetric with one five-co-ordinate and one four-co-ordinate cobalt(II) atom. The bidentate dppe ligand is chelated to Co(1) with a mean Co(1)–P bond length of 2.21(2) Å, which is shorter than that of 2.27(2) Å found in $[Co(dppe)_2Cl]^+$ for a five-co-ordinated cobalt(II).[3] The mean Co(2)–S_b† bond length of 2.29(2) Å compares with the corresponding value of 2.32(1) Å found in $[(\mu_2\text{-}SPh)_6(CoSPh)_4]^{2-}$.[4] The Co–Co atomic distance of 2.635(3) Å is longer than 2.541 Å in $[Co_2(dppe)(CO)_6]$, but is considerably shorter than 3.03(1) Å found in $[Co_2(SEt)_6]^{2-}$.[5]

The weak Co ESR signals and relatively low paramagnetic moment (3.69 μ_B) at room temperature indicate partial magnetic coupling between two paramagnetic centres, Co^{II} ions, in the asymmetrical dicobalt compound.

We acknowledge support (in part) by the National Natural Science Foundation.

Received, 5th July 1989; Com. 9/02867F

References

1 G. R. Van Hecke and W. D. Horrocks, Jr., *Inorg. Chem.*, 1966, **5**, 1960; W. D. Horrocks, Jr., G. R. Van Hecke, and D. W. Hall, *ibid.*, 1967, **6**, 694; L. Sacconi, *J. Chem. Soc. (A)*, 1970, 248; M. Atoh, I. Kinoshita, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 3179; R. P. Aggarwal, N. G. Connelly, M. C. Crespo, B. J. Dunne, P. M. Hopkins, and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1989, 33.
2 S. W. Carr and R. Colton, *Aust. J. Chem.*, 1981, **34**, 35.
3 J. K. Stalick, P. W. R. Corfield, and D. W. Meek, *Inorg. Chem.*, 1973, **12**, 1668.
4 I. G. Dance, *J. Am. Chem. Soc.*, 1979, **101**, 6264.
5 K. S. Hagen and R. H. Holm, *Inorg. Chem.*, 1984, **23**, 418.

---

‡ *Crystal data* for $C_{50}H_{44}Co_2P_2S_4$: $M = 952.7$, triclinic, space group $P\bar{1}$, $a = 11.359(2)$, $b = 11.481(3)$, $c = 17.639(2)$ Å, $\alpha = 99.37(2)$, $\beta = 90.89(1)$, $\gamma = 93.84(2)°$, $U = 2263.6$ Å^3, $Z = 2$, $D_c = 1.397$ g cm^{-3}; $\mu = 10.1$ cm^{-1}; 7338 independent reflections measured, 2878 reflections with $I > 3\sigma(I)$ used in refinement. Determination of cell constants and data collection were carried out at room temperature with Mo-K_α radiation with a Nonius CAD-4 diffractometer equipped with a graphite monochromator. Data were recorded by a θ–2θ scan in the range $1 < \theta < 24°$ and were corrected for Lorentz-polarization effects and empirical absorption based upon a scan. The structure was solved by direct methods and refined by full-matrix least-squares with anisotropic thermal parameters for Co, S, and P atoms. DIFABS technique was used in the process to a final conventional factor $R = 0.066$ and $R_w = 0.083$. All calculations were carried out on a VAX 11/785 computer with the SDP program package. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.