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Crystal and Molecular Structure of Bis(1-diphenylphosphinothioyl-3-methylthioureato)nickel(II)

Toschitake IWAMOTO,* Fujio EBINA, Hiroshi NAKAZAWA, and Chiaki NAKATSUKA

Department of Chemistry, College of General Education, The University of Tokyo, Komaba, Meguro, Tokyo 153

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Synopsis. The title compound [Ni{$(C_6H_5)_2$PSNCSNHCH$_3$}$_2$] was found to crystallize in the monoclinic space group C2/c with a=23.29(1), b=9.457(2), c=16.40(1) Å, β=121.33(8)°, Z=4. The six-membered chelate ring built of five kinds of atoms, Ni, 2S, P, N, and C, was demonstrated.

Ojima *et al.*[1,2] proposed that some diphenylphosphinothioylthioureatometal(II) complexes have a chelate structure consisting of five kinds of atoms, M(II), 2S, P, N, and C. In order to confirm the existence of such a chelate ring, the title compound was subjected to X-ray structural analysis.

Experimental

Among the complexes reported,[1,2] a complex previously described as bis(3-diphenylphosphinothioyl-1,1-dimethylthioureato)nickel(II) was chosen because of its good appearance as fine crystals. A 0.2×0.4×0.6 mm single crystal grown up from a dichloromethane–ethanol solution was used for the X-ray diffraction experiments. In the course of structure refinement, the crystal was confirmed to be that of the title compound, bis(1-diphenylphosphinothioyl-3-methylthioureato)nickel(II). After preliminary Weissenberg photographs were taken, precise determination of lattice parameters and collection of intensity data were carried out on a Rigaku automated four-circle diffractometer using Cu $K\alpha$ radiation, the procedure being similar to that reported.[3] Of 4142 observed reflections with $2\theta \leq 120°$, 1671 with $|F_o| \geq 3\sigma(|F_o|)$ were used for the structure refinement. The absorption corrections[4] were applied together with Lp ones. The density was measured by the flotation method using potassium tetraiodomercurate solution. Crystal data: $NiC_{28}H_{28}N_4P_2S_4$, $F.W.$=669.44. Monoclinic, space group C2/c, a=23.29(1), b=9.457(2), c=16.40(1) Å, β=121.33(8)°, Z=4. D_m=1.45, D_x=1.44 g cm^{-3}. Systematic absences: hkl, $h+k=2n+1$; $h0l$, $l=2n+1$. μ(Cu $K\alpha$)=45.36 cm^{-1}.

The structure was solved by the heavy-atom method. All the calculations were carried out on a HITAC 8800/8700 computer at the Computatinon Center of this University. The programs used were those in UNICS[5] and their local versions. The atomic scattering factors were taken from those of Cromer and Waber.[6] From the three-dimensional Patterson synthesis, the Ni atoms were located at the inversion centers in the c glide planes. In successive Fourier syntheses, the positions of all the remaining non-hydrogen atoms could be found out except that of the second methyl-C atom should have been found for the dimethyl compound around the N(2) atom of the side chain. Since the measured density was smaller by 0.02 g cm^{-3} than that calculated for the dimethyl compound, the refinement was progressed assuming this crystal to be that of the title compound. Several cycles of block-diagonal least-squares calculations were carried out to the final R=0.093, the real and imaginary parts of the anomalous dispersion

TABLE 1. POSITIONAL AND THERMAL PARAMETERS FOR [Ni{$(C_6H_5)_2$PSNCSNHCH$_3$}$_2$][a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	5000	5000	5000	11(1)	23(1)	19(1)	−2(1)	6(1)	−2(1)
S(1)	4786(1)	4419(2)	3560(1)	17(1)	40(1)	21(1)	−3(1)	8(1)	−5(1)
S(2)	3948(1)	5125(2)	4664(1)	13(1)	28(1)	29(1)	−3(1)	10(1)	−6(1)
P	3555(1)	3349(2)	3889(1)	13(1)	25(1)	23(1)	−3(1)	8(1)	−2(1)
N(1)	3529(3)	3260(7)	2890(4)	26(4)	41(4)	27(3)	−9(3)	14(3)	−4(2)
N(2)	3908(4)	3545(8)	1869(4)	30(4)	61(4)	19(3)	−14(3)	12(3)	−10(3)
C(1)	4000(4)	3668(8)	2747(4)	32(5)	28(4)	22(3)	0(4)	12(3)	−3(3)
C(2)	3272(5)	2920(12)	1092(5)	53(6)	91(7)	23(4)	−39(6)	12(4)	−18(4)
C(11)	2966(4)	3230(7)	3587(4)	7(4)	35(4)	22(3)	−5(3)	4(3)	0(3)
C(12)	2494(4)	3796(10)	4179(5)	27(5)	55(5)	40(4)	−8(4)	19(4)	−11(4)
C(13)	1839(4)	3637(11)	3966(6)	12(4)	73(6)	57(5)	−14(5)	23(4)	−7(4)
C(14)	1390(4)	2842(10)	3196(6)	26(5)	59(6)	43(5)	−4(4)	13(4)	−1(4)
C(15)	1590(4)	2261(11)	2599(6)	14(4)	63(6)	53(5)	−18(4)	9(4)	−13(4)
C(16)	2231(4)	2480(10)	2783(6)	28(5)	52(5)	42(4)	−12(4)	18(4)	−18(4)
C(21)	3955(4)	1788(8)	4574(5)	17(4)	27(4)	46(4)	1(3)	27(4)	4(3)
C(22)	3721(5)	475(10)	4132(6)	46(6)	37(5)	59(6)	−6(5)	32(5)	−12(4)
C(23)	4006(6)	−759(10)	4645(7)	92(9)	33(5)	71(7)	9(5)	45(6)	8(4)
C(24)	4536(5)	−690(10)	5606(8)	40(6)	40(5)	102(8)	15(5)	52(6)	21(5)
C(25)	4757(5)	580(10)	6030(7)	24(5)	57(6)	66(6)	10(5)	24(4)	24(4)
C(26)	4480(4)	1851(9)	5533(5)	19(4)	43(4)	44(4)	9(4)	15(4)	12(3)

a) The positional and thermal parameters have been multiplied by 10^4 and 10^3, respectively, the numbers in parentheses being esd's in the last signigicant digits. The form of thermal parameters is $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*\cos\beta^*+2U_{23}klb^*c^*)]$.

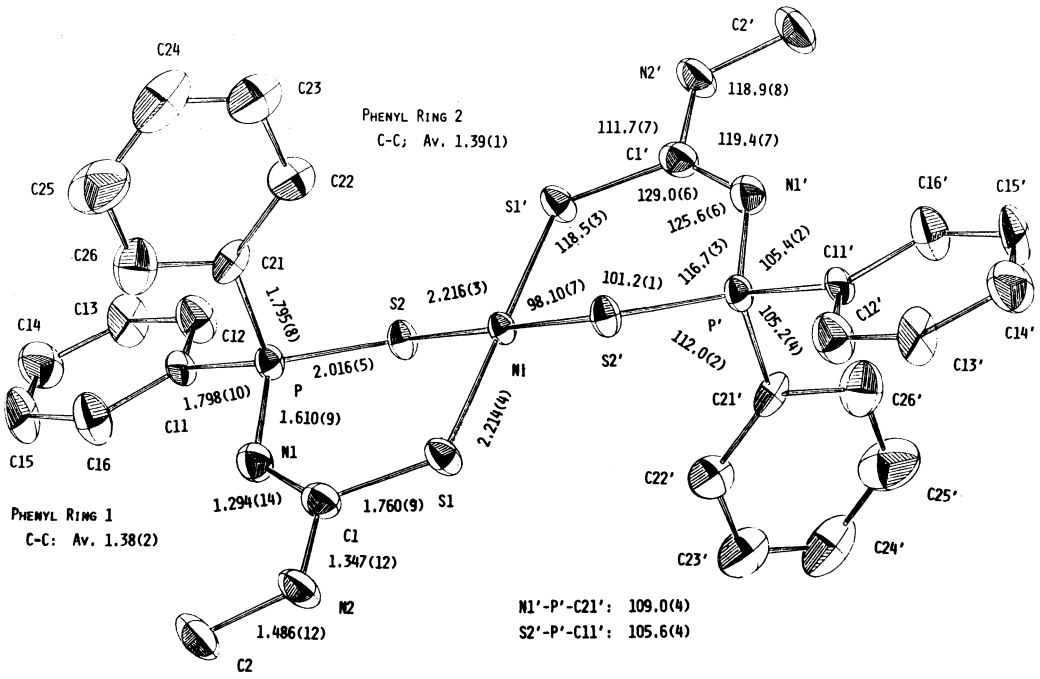

Fig. 1. An ORTEP view of $[Ni\{(C_6H_5)_2PSNCSNHCH_3\}_2]$ molecule using 50% probablity ellipsoids. The bond distances and angles are given in Å and degree, respectively, and the numbers in parentheses are esd's in the last significant digits.

correction being also made.[7] The shift of each atomic parameter was within one-third of the estimated standard deviation at the last two cycles. The final difference Fourier map showed no significant peak attributable to the "second" methyl-C atom. This shows that the analyzed crystal is composed of the title compound. The refinement with the Cc space group, another possible one for the observed systematic absences, afforded no improvement.

Description of the Structure

The final atomic parameters are given in Table 1. The molecular structure of the complex is shown in Fig. 1 with the values of important bond distances and angles. The Ni atom is bonded to S(1) and S(2) atoms of the ligands in a square-planar trans configuration. The six-membered chelate ring is built of Ni, S(1), C(1), N(1), P, and S(2) atoms as proposed by Ojima *et al.*[1,2] The chelate ring, the phenyl ring 1, and the methylamino side chain are roughly parallel to the ac plane, and the phenyl ring 2 protrudes from the P atom of the chelate ring into a direction approximately parallel to the b axis. The NiS_4 coordination sphere resembles that in bisdithioacetylacetonatonickel(II)[8] and other conjugated bis(thioketo-thiolato)nickel(II) complexes. The chelate ring has the following features of bond distances. The average Ni–S bond length 2.215 Å is longer than those in the conjugated thioketo-thiolato type complexes. The C(1)–S(1) bond is comparable in length to that in bismaleonitrildithiolatonickelate(II).[9] The P–S(2) and P–N(1) bonds appear to be partially double. The N(1)–C(1) bond is too short for a C=N bond. Although these features could support a partial conjugation of π-orbitals in the chelate ring, the unfavorable deviations of the relevant atoms from the calculated best plane are: P 0.59, N(1) 0.19, Ni 0.08, C(1) −0.11, S(1) −0.16, and S(2) −0.47 Å.

References

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3) T. Iwamoto and M. Kiyoki, *Bull. Chem. Soc. Jpn.*, **48**, 2414 (1975).

4) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham Vol. II, p. 291. The crystal elongated along b axis could not be cut down into smaller pieces.

5) Universal Crystallographic Computation Program System (UNICS), ed by T. Sakurai, Crystallographic Society of Japan, Tokyo (1967).

6) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV.

7) The table of the structure factors is kept as Document No. 7920 at the Chemical Society of Japan.

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9) R. Eisneberg and J. A. Ibers, *Inorg. Chem.*, **4**, 605 (1965).