Inorganica Chimica Acta, 22 (1977) L17–L18

Crystal and Molecular Structure of the Binuclear Complex $[2Ni(acac)_2]Ph_3AsO$

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Received February 5, 1977

The reaction of bis(2:4 pentanedionato)nickel(II), $[Ni(acac)_2]$, with triphenylarsine oxide (Ph_3AsO) in ethanol yields a green crystalline product with 2:1 Ni:As stoichiometry, $[2Ni(acac)_2]Ph_3AsO$. The visible spectrum and magnetic moment (μ_{eff} = 3.16 BM) of the compound are typical of octahedrally coordinated nickel(II). The corresponding reaction with $[Co(acac)_2]$ yields a less well defined product, of variable analytical composition, but it is usually possible to separate manually a few well-formed, deep pink crystals which prove on X-ray examination to be isomorphous with those of the nickel compound. In order to establish unequivocally the coordination of the metal atoms and to determine the function of the arsine oxide ligand we have carried out an X-ray crystal structure determination for the nickel complex.

Crystal data. $[2Ni(acac)_2]Ph_3AsO$. Found: C, 54.9; H, 5.2; Ni, 14.1%. Calc. for $C_{38}H_{43}AsNi_2O_9$: C, 54.6; H, 5.2; Ni, 14.0%. Monoclinic, $P2_1/_a$; a = 18.12, b = 12.4, c = 18.98 Å, β = 117.5°; Z = 4.

A total of 926 independent reflections were measured and used in the structure determination. The approximate atom positions were identified by the usual processes of Patterson and Fourier synthesis and refined by successive cycles of least-squares analysis [1] until the shifts after each cycle were less than 0.1 ESD and no significant features appeared on a difference map. In the final stages of the refinement, anisotropic temperature factors were employed for the nickel and arsenic atoms: the relatively small number of reflections available did not permit anisotropic refinement of the lighter atom positions. The final value of R was 0.0595; the hydrogen atoms were not located.

The essential features of the structure are illustrated in Fig. 1. For clarity, the four 2:4 pentanedionato ligands are indicated as L(1), L(2), L(3) and L(4) and the phenyl groups of the Ph_3AsO ligand are omitted.

The molecule is binuclear with three Ni–O–Ni bridges; in effect, it consists of two NiO_6 octahedra with a common face. The arsine oxide oxygen atom O(1) occupies the apical position, the other two Ni–O–Ni bridges being formed by oxygen atoms [O(5) and O(7)] from the ligands L(2) and L(3). The second oxygen atoms in these ligands [O(4), O(6)] are attached to Ni(1) and Ni(2), respectively. The ligand L(1) is bound exclusively to Ni(1) and L(4) to Ni(2). The points of attachment of the pentanedionato ligands in the two halves of the molecule are not symmetry-related, and the molecule as a whole is asymmetric.

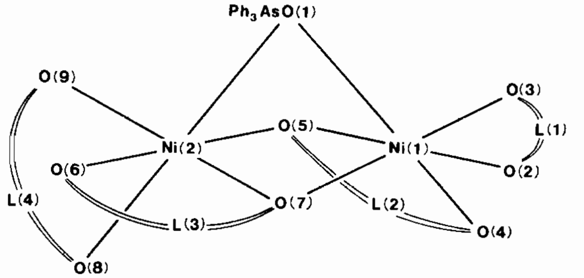

Fig. 1. The essential features of the structure.

TABLE I. Selected Bond Lengths and Angles.

Bond Lengths (ESD in final significant figure), (Å)			
Ni(1)–O(1)	2.28(1)	Ni(2)–O(1)	2.11(2)
Ni(1)–O(5)	2.00(2)	Ni(2)–O(5)	2.21(2)
Ni(1)–O(7)	2.06(2)	Ni(2)–O(7)	2.03(1)
Ni(1)–O(2)	1.98(2)	Ni(2)–O(6)	1.98(2)
Ni(1)–O(3)	1.96(2)	Ni(2)–O(8)	1.98(2)
Ni(1)–O(4)	2.03(1)	Ni(2)–O(9)	1.95(2)
Ni(1)–Ni(2)	2.901(4)		
As–O(1)	1.62(2)		
As–C(mean)	1.91		
Bond Angles (ESD 0.6°)			
O(1)–Ni(1)–O(5)	75.2	Ni(1)–O(1)–Ni(2)	82.6
O(1)–Ni(1)–O(7)	77.5	Ni(1)–O(5)–Ni(2)	86.7
O(5)–Ni(1)–O(7)	81.5	Ni(1)–O(7)–Ni(2)	90.3
O(1)–Ni(2)–O(5)	74.6		
O(1)–Ni(2)–O(7)	82.3	O(1)–Ni(1)–O(4)	165.9
O(5)–Ni(2)–O(7)	77.2	O(1)–Ni(2)–O(8)	167.7

Two of the three oxygen bridges are significantly distorted. The oxygen atom O(1) is displaced towards Ni(2) and O(5) is displaced towards Ni(1) [Table I]. The third atom, O(7) is more nearly midway between the two nickel atoms. The reason for this distortion is not entirely clear but it may arise from unequal nonbonded interactions between the pentanedionato ligands and the three phenyl rings of the arsine oxide. The NiO_6 octahedra are appreciably distorted towards the shared face, with the result that the angles subtended at the nickel atoms by the bridging oxygen atoms are all appreciably less than 90°. The angles subtended by the terminal oxygen atoms are all within the range 92 ± 2°. The Ni–Ni distance across

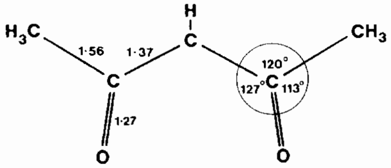

Fig. 2. The average dimensions of the pentanedionato ligands.

the shared face is 2.901 Å, suggesting that some degree of antiferromagnetic coupling may be detectable at low temperatures.

The average dimensions of the coordinated pentanedionato ligands are indicated in Fig. 2. The average C–C bond length in the phenyl rings is 1.39 Å and the As–O and As–C bond lengths are similar to those measured in other triphenylarsine oxide complexes [2–4].

Bridging Ph_3AsO ligands were first positively identified in the dimeric mercury complex $[HgCl_2 \cdot Ph_3AsO]_2$ [2]. The As–O stretching absorption in the i.r. spectrum of this complex occurs at the unusually low frequency of 810 cm^{-1}: in complexes containing terminally bonded Ph_3AsO the As–O stretch usually appears between 880–835 cm^{-1} [4]. In $[2Ni(acac)_2] \cdot Ph_3AsO$, however, the As–O stretch occurs at 842 cm^{-1}, near the lower end of the 'terminally bonded' frequency range and appreciably above the frequency in $[HgCl_2 \cdot Ph_3AsO]_2$. Thus infrared data alone cannot be used reliably to distinguish between bridging and non-bridging Ph_3AsO ligands.

Full details of the structure of this and the isomorphous cobalt(II) complex will be published.

References

1 Crystallographic programmes were those of F. R. Ahmed *et al.*, N.R.C., Ottawa, adapted by J. S. Knowles and H. F. W. Taylor for use on the ICL System 4/70 computer.
2 C.-I. Branden, *Arkiv. Kemi, 22,* 485 (1964).
3 C.-I. Branden, *Acta Chem. Scand., 17,* 1363 (1963).
4 R. Graziani, B. Zarli, G. Bombieri, E. Forsellini and E. Tondello, *Inorg. Chem., 9,* 2116 (1970).
5 D. Phillips and S. Y. Tyree, *J. Am. Chem. Soc., 83,* 1806 (1961).