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Nickel(II) Cyanide–Diisopropyl Methylphosphonate 1:1 Adduct

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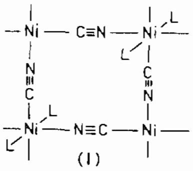
Although complex formation between neutral phosphonate or phosphate alkylesters and metal salts occurs readily in solution [1–3] or by vapor–solid interaction (*in vacuo*) [1, 4, 5] as clearly demonstrated [6] by negative $\nu_{P=O}$ frequency shifts [1–5], the isolation of these complexes in the solid state is generally difficult, and not always possible [1]. Thus, in the case of diisopropyl methylphosphonate (DIMP; $(i\text{-}C_3H_7O)_2CH_3P=O$), metal perchlorate, thiocyanate or nitrate complexes are initially obtained in the presence of triethyl orthoformate (TEOF) in the form of viscous oils, the solidification of which requires rather tedious procedures [3]. Whereas, during metal halide–DIMP interactions, the formation of polynuclear metal complexes with ligands produced by partial or complete depropylation of DIMP (accompanied by simultaneous evolution of isopropyl halide) is generally favored [1, 7–9]. Attempts at the isolation of solid DIMP–metal halide adducts have been unsuccessful in most cases [1, 3, 8, 9]. The only reported adducts of DIMP with metal halides are those with Sn^{2+}, Sn^{4+} and Ti^{4+} halides [7], LiI [9], and $MgCl_2$–MCl_2 (M = Mn, Fe, Co, Ni, Cu, Zn) equimolar mixtures [3].

In light of the preceding information, the fact that, during DIMP–$Ni(CN)_2$ interaction, a solid complex analyzing as $Ni(CN)_2\cdot$DIMP (analysis by Schwarzkopf, Woodside, N.Y.; found (calc.)%: Ni 20.40(20.18); C 36.97(37.16); H 5.83(5.89); P 10.52(10.65); N 9.75(9.63)), was quite easily obtained in 100% yield (on the basis of the $Ni(CN)_2$ present), was somewhat surprising. This product, which can be prepared either in the atmosphere or under N_2 was synthesized as follows: 1 g $Ni(CN)_2$ was suspended in *ca.* 50 ml of a 1:1 vol/vol) DIMP–TEOF mixture, and the temperature of the resulting suspension was increased at a rate of 5 °C/min, from ambient to *ca.* 90 °C, under gentle stirring. No reaction was observed at temperatures up to 80 °C, but in the 80–90 °C region the mixture was abruptly converted into a thick gelatinous light blue–green mass, which was suspended in *ca.* 100 ml TEOF and filtered. The new complex was obtained as a light blue–green powder on the filter, and after being thoroughly washed with anhydrous diethyl ether, it was stored in an evacuated dessicator over $CaCl_2$. It is air-stable, apparently polymeric (insoluble in all common organic solvents), and decomposes at 230 °C (change of color to brown) without melting.

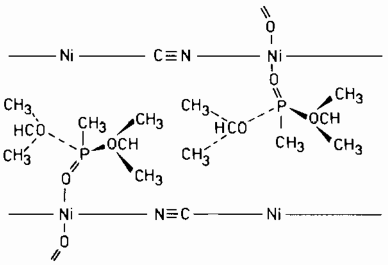
Free DIMP shows the $\nu_{P=O}$ mode at 1241 cm^{-1} (strong) [3–5], whilst ν_{CN} in anhydrous $Ni(CN)_2$ occurs at 2176 cm^{-1} (strong) [10]. DIMP also shows the following additional bands at 1310–785 cm^{-1} [3, 11]: 1309m (ν_{PCH_3}), 1173m, 1139m, 1106m (all three due to $\nu_{C-O-(P)}$, 1008 vs, 980 vs (both $\nu_{P-O-(C)}$), 912m, 895m (both ν_{PCH_3}), 787m ($\nu_{P-O-(C)}$). The new complex shows the $\nu_{P=O}$ and ν_{CN} modes at 1212 and 2169 cm^{-1}, respectively (strong bands); the rest of the DIMP bands at 1310–785 cm^{-1} remain practically unchanged, upon complex formation with $Ni(CN)_2$, *viz.*: 1309m, 1173m, 1140m, 1107m, 1011vs, 984vs, 912m, 896m, 791s. The negative $\nu_{P=O}$ frequency shift (by 29 cm^{-1}) demonstrates that DIMP is coordinated through the P=O oxygen [1–6], while the insensitivity of the $\nu_{C-O-(P)}$ and $\nu_{P-O-(C)}$ modes to complex formation rules out the possibility [12] of simultaneous bonding of the ligand through one of the alkoxy oxygens. The infrared spectrum of the new complex is devoid of bands attributable to the presence of water (ν_{OH}, δ_{H-O-H} modes) [13]. The magnetic moment of the complex is 2.36 μB at 297 °K, and its solid-state (Nujol mull) electronic spectrum shows the following maxima (nm): 264vvs, 283vvs, 308vs,b, 402s,sh, 461m,sh, 602m–w, 722w,sh, 948s,b, 1070w,b. These magnetic and electronic spectral properties are very similar to those observed for a series of polymeric $Ni(CN)_2$ 1:1 adducts with ligands such as water, ammonia and alkylamines [13–19]. Water or ammonia 1:1 adducts with $Ni(CN)_2$ consist of layers of polymeric units of type (I) (L = H_2O, NH_3), involving alternating diamagnetic square-planar



(I)

and paramagnetic octahedral Ni^{2+} ions (NiC_2N_2 and $NiC_2N_2L_2$ moieties, respectively). These compounds have the tendency to form clathrates by inclusion of uncoordinated molecules, such as benzene, pyrrole, furan, thiophene, phenol and water, between parallel layers of type (I) [13–18]. When, however, L is a larger molecule, such as a primary long-chain alkylamine, the adduct consists of alternating monolayers of type (I) (with the amine nitrogens coordinated to Ni^{2+} ions) and the hydrocarbon moiety of the amine [19].

The overall evidence available for the new complex points out to a structure similar to that of the primary n-alkylamine analogs [19]. In fact, the low μ_{eff} value (2.36 μB) observed, is obviously due to the presence of alternating square-planar (NiC_2N_2 moieties) and octahedral ($NiC_2N_2O_2$ moieties) Ni^{2+} ions as in (I); a normal magnetic moment of 3.33 μB is calculated ($\sqrt{2} \times 2.36$) [13] by assuming that only half of the Ni(II) present is high-spin (S = 1), while the other half is low-spin (S = 0). The electronic spectral bands at 264–308 nm are assigned as the $^1A_{1g} \rightarrow {}^1E_u$, $^1A_{2u}$ and $^1B_{1u}$ transitions of square-planar Ni^{2+}, respectively [13, 17, 20] (these transitions presumably overlap with ligand bands in this region [8], while those at 406–1070 nm are due to the $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, $^3T_{1g}(F)$, $^1E_g(D)$ and $^3T_{2g}(F)$ transitions of octahedral Ni^{2+} [13, 17]; the splittings observed in the latter region are suggestive of a symmetry lower than O_h for the hexacoordinated Ni^{2+} ions [21]. DIMP behaves as a unidentate O-ligand, as shown by the negative $\nu_{P=O}$ frequency shift; two DIMP ligands, *trans* to each other, are coordinated to every other Ni^{2+} ion, occupying the coordination sites above and below the NiC_2N_2 plane. On the other hand, the occurrence of ν_{CN} at 2169 cm^{-1} is consistent with a cyano-bridged polymeric structure [10, 13, 15, 22] rather than one involving monomeric $[Ni(CN)_4]^{2-}$ anions, which exhibit the strongest ν_{CN} absorption at 2135–2125 cm^{-1} [10, 23]. Hence, the new complex appears to consist of parallel layers of units of type (I) (L = DIMP), with the tetrahedral organophosphoryl molecules encaged between these layers. A possible arrangement of the DIMP ligands between the Ni(II) cyanide layers is shown in (II) (edge-on view). The presence of nonlinear Ni–O–P groupings is assumed, since this appears to be a general phenomenon in metal complexes with $R_3P=O$ ligands [1, 24].



(II)

These laboratories are planning to explore the possibility of preparing and characterizing complexes similar to that herein reported, by studying the interactions of several organophosphoryl (neutral phosphate, phosphonate and phosphinate esters and triorganophosphine oxides, with a variety of substituents, *e.g.*, n-C_1 to C_8 alkyls, branched alkyls, aryls, bis(dialkylamino) groups) and other "oxo"- (N-oxides, sulfoxides *etc.*) ligands with Ni(II) and other metal cyanides.

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References

1 N. M. Karayannis, C. M. Mikulski and L. L. Pytlewski, *Inorg. Chim. Acta Rev., 5,* 69 (1971).

2 D. F. C. Morris, E. L. Short and D. N. Slater, *Electrochim. Acta, 8,* 289 (1963).

3 N. M. Karayannis, C. Owens, L. L. Pytlewski and M. M. Labes, *J. Inorg. Nucl. Chem., 31,* 2059 (1969); *32,* 83 (1970).

4 G. G. Guilbault and J Daś, *J. Phys. Chem., 73,* 2243 (1969).

5 G G. Guilbault and E. P. Scheide, *J. Inorg. Nucl. Chem., 32,* 2959 (1970); E. P. Scheide and G. G. Guilbault, *ibid., 33,* 1869 (1971).

6 F. A. Cotton, R. D. Barnes and E. Bannister, *J. Chem. Soc.,* 2199 (1960).

7 C. Owens, N. M. Karayannis, L. L. Pytlewski and M. M. Labes, *J. Phys. Chem., 75,* 637 (1971).

8 C. M. Mikulski, N M. Karayannis, J. V. Minkiewicz, L. L. Pytlewski and M. M. Labes, *Inorg. Chim. Acta, 3,* 523 (1969).

9 N. M. Karayannis, C. M. Mikulski, M. J. Strocko, L. L. Pytlewski and M. M. Labes, *Inorg. Chim. Acta, 5,* 357 (1971); *Z. anorg. allg. Chem., 384,* 267 (1971).

10 M. F. A. El-Sayed and R. K. Sheline, *J. Am. Chem. Soc., 78,* 702 (1956); *J. Inorg. Nucl. Chem., 6,* 187 (1958); D. A. Dows, A. Haim and W K. Wilmarth, *ibid., 21,* 33 (1961).

11 L. C. Thomas and R. A. Chittenden, *Spectrochim. Acta, 20,* 467, 489 (1964); *21,* 1905 (1965).

12 O. A. Osipov, V. I. Gaivoronskii and A. A. Shvets, *Zh. Neorg. Khim., 8,* 2190 (1963).

13 A. Ludi and R. Hügi, *Helv. Chim. Acta, 50,* 1283 (1967); *51,* 349 (1968).

14 K. A. Hofmann and F. Küspert, *Z. anorg. Chem., 15,* 204 (1897); K. A. Hofmann and F. Höchtlen, *Ber. deutsch. Chem. Ges., 36,* 1149 (1903); K. A. Hofmann and H. Arnoldi, *ibid., 39,* 339 (1906).

15 R. S. Drago, J. T. Kwon and R. D. Archer, *J. Am. Chem. Soc., 80,* 2667 (1968).

16 J. H. Rayner and H. M. Powell, *J. Chem. Soc.,* 319 (1952); 3412 (1958); M. A. Porai-Koshits, *Zh. Strukt. Khim., 1,* 125 (1960).

17 E. E. Aynsley and W. A. Campbell, *J. Chem. Soc.,* 4137 (1957); 1723 (1958).

18 Y. Mathey and C. Mazières, *Can. J. Chem., 52,* 3637 (1974).

19 A. Weiss and R. Frank, *Kolloid-Z., 177,* 47 (1961); J. Cano-Ruiz, J. M. Esteban Bermudez and E. Gutierrez Rios, *Anales Real Soc. Espan. Fis. Quim., 61B,* 1055 (1965); G. F. Walker and D. G. Hawthorne, *Trans. Faraday Soc., 63,* 166 (1966).

20 H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc., 85,* 260 (1963).

21 W. Byers, A. B. P. Lever and R. V. Parish, *Inorg. Chem., 7,* 1835 (1968).

22 D. F. Shriver, S. A. Shriver and S. E. Anderson, *Inorg. Chem., 4,* 725 (1965); V. M. Bhatnagar, *Zh. Strukt. Khim., 8,* 698 (1967); R. Nast, H. Ruppert-Mesche and M. Helbig-Neubauer, *Z. anorg. allg. Chem., 312,* 314 (1961).

23 R. L. McCullough, L. H. Jones and G A. Crosby, *Spectrochim. Acta, 16,* 929 (1960).

24 F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc., 85,* 2402 (1965); G. Bombieri, U. Croatto, E. Forsellini, B. Zarli and R. Graziani, *J. Chem. Soc. Dalton,* 560 (1972); M. M. Mangion, R. Smith and S. G. Shore, *Cryst. Struct. Commun., 5,* 493 (1976).