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Inorganic Chemistry Communications 7 (2004) 38-41

INORGANIC CHEMISTRY COMMUNICATIONS

www.elsevier.com/locate/inoche

Solid state and solution structures of the nickel(II) complex NiL₂ of the ambidentate (S,S)- or (P,S)-chelating ligand 3-diphenylphosphane-carbothioyl-1,1-dimethyl-thiourea (HL)

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Received 18 August 2003; accepted 2 September 2003 Published online: 31 October 2003

Abstract

The ambidentate (S,S)- or (P,S)-bidentate ligand, 3-diphenylphosphane-carbothioyl-1,1-dimethyl-thiourea (HL), has been prepared, and the solid state and solution structures of its nickel(II) complex, NiL₂, investigated. In the solid state the nickel(II) centre is square-planar and the ligand is coordinated in the (S,S)-bidentate mode, whereas in chloroform solution an equilibrium mixture of three isomers is rapidly formed, in which a (P,S)-bidentate species is the major component. © 2003 Elsevier B.V. All rights reserved.

Keywords: Nickel(II); Ambidentate ligands; Dithiobiuret; Phosphines

1. Introduction

The dithiobiurets are amongst the simplest, and least odoriferous, (S,S)-bidentate ligands available to coordination chemistry, and a wide range of derivatives are easy to prepare by straightforward methods [1–4]. Despite being thioamides, dithiobiurets are good ligands for transition metal ions for two simple reasons: the central NH group is acidic and readily deprotonates to give a delocalised anionic ligand (cf. acetylacetonate), and the lone pairs of the two terminal R₂N groups are delocalised into the thiocarbonyl groups. As a consequence there are several resonance structures for the dithiobiuret anion in which the sulphur atoms are formally anionic.

Surprisingly, the replacement of one (or both) of the terminal R_2N groups in dithiobiuret-type ligands with R_2P groups has not been reported. The phosphorus lone pair would be expected to be very much less delocalised

into the adjacent thiocarbonyl group and thus reduce the latter's donor ability as a ligand. However, the corollary of this is that the R_2P group is available to coordinate to the metal centre instead of the thiocarbonyl group; i.e., the system may act as a (P,S)-bidentate ligand. The coordinating behaviour of these potentially ambidentate ligands will necessarily depend upon a subtle balance of steric and electronic factors, as well as the nature of the metal ion. We herein report the synthesis of such a R_2P -containing dithiobiuret analogue, 3-diphenylphosphane-carbothioyl-1,1-dimethyl-thiourea (HL), and the solid state and solution structures of its homoleptic nickel(II) complex, NiL₂.



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^{1387-7003/\$ -} see front matter \odot 2003 Elsevier B.V. All rights reserved. doi:10.1016/j.inoche.2003.09.021

2. Experimental

2.1. Synthesis of $NiL_2 \cdot CH_2Cl_2$

Under an atmosphere of dinitrogen, dimethylthiocarbamoyl chloride (1.24 g, 10 mmol) was added dropwise (5 min) with stirring to a solution of potassium thiocyanate (0.98 g, 10 mmol) in dry acetonitrile (40 cm^3) . During the addition a fine white precipitate of potassium chloride was formed. After 30 min diphenylphosphine (1.87 g, 10 mmol) was added and the solution stirred for a further 15 min, then nickel(II) acetate tetrahydrate (1.25 g, 5 mmol) added and the reaction mixture instantly became dark brown. The crude product was precipitated with water (200 cm³), isolated by filtration, dried in air and recrystallised from dichloromethane/ethanol as brown crystals of $NiL_2 \cdot CH_2Cl_2$; yield 1.45 g (36%). The compound slowly loses the dichloromethane of crystallisation upon standing. Anal. Calc. for $C_{33}H_{34}Cl_2N_4NiP_2S_4$ (MW = 806.44): C, 49.15; H, 4.12; N, 6.95; S, 15.90%. Found: C, 48.84; H, 4.20; N, 6.88; S, 15.65%. ¹H NMR (400 MHz, CDCl₃): δ 7.95 (III, 4H, m, ArH), 7.79 (IV, 4H, m, ArH), 7.57-7.27 (m, ArH), 3.38 (IV, 3H, s, CH₃), 3.35 (III, 3H, s, CH₃), 3.31 (IV, 3H, s, CH₃), 3.26 (I/II, 3H, br s, CH₃), 3.22 (III, 3H, s, CH₃), 2.83 (IV, 3H, s, CH₃), 2.79 (III, 3H, s, CH₃), 2.72 (III, 3H, s, CH₃), 2.69 (IV, 3H, s, CH₃), 2.64 (I/II, 3H, br s, CH₃). ³¹P NMR (162.07 MHz, CDCl₃): δ 24.72 (III, d, ${}^{4}J_{PP(trans)} = 14$ Hz), 21.95 (I/II or IV, s), 20.48 (I/II or IV, s), -20.74 (III, d, ${}^{4}J_{PP(trans)} = 14$ Hz), -21.63 (IV, s). v_{max} (cm⁻¹): 1470(s) 1433(m), 1382(s), 1278(m), 1185(w), 1125(m), 1025(w), 998(w), 920(w), 897(m), 738(m), 691(m), 568(w), 497(w), 477(w), 440(w).

3. Results and discussion

The ligand, 3-diphenylphosphanecarbothioyl-1,1-dimethyl-thiourea (HL), was readily prepared in situ by the reaction of dimethylthiocarbamoyl isothiocyanate with diphenylphosphine in acetonitrile (Scheme 1). The free ligand was not isolated, but was complexed immediately with nickel(II). The brown nickel(II) complex, NiL₂, crystallises as a single isomer, but ¹H and ³¹P NMR



Scheme 1. Synthesis of HL and NiL_2 .

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Fig. 1. ORTEP view of the molecular structure of NiL₂ with thermal ellipsoids shown at 50% [7]. Selected bond lengths (Å) and angles (°): Ni(1)–S(1), 2.1548(6); Ni(1)–S(2), 2.1668(6); S(1)–C(1), 1.704(2); S(2)–C(2), 1.725(2); P(1)–C(1), 1.858(2); P(1)–C(5), 1.826(2); P(1)–C(11), 1.831(2); N(1)–C(2), 1.333(3); N(1)–C(3), 1.460(3); N(1)–C(4), 1.471(3); N(2)–C(1), 1.298(3); N(2)–C(2), 1.358(3); S(1)–Ni(1)–S(2), 97.04(2); Ni(1)–S(1)–C(1), 115.73(8); Ni(1)–S(2)–C(2), 116.90(8); S(1)–C(1)–N(2), 133.34(18); S(2)–C(2)–N(2), 129.07(17); C(1)–N(2)–C(2), 126.6(2).

spectroscopy showed that it exists as an equilibrium mixture of three species in chloroform solution at room temperature (vide supra); the same equilibrium mixture in solution was also obtained after repeated recrystallisation of the compound, and by dissolving large, X-ray quality, single crystals.

The X-ray structure ¹ of NiL₂ (Fig. 1) shows that it crystallises as a single isomer (isomer I) from dichloromethane/ethanol, presumably because this isomer has the lowest solubility under these conditions. The nickel(II) centre has a square-planar geometry with a *trans* arrangement of the two ligands and the phosphorus atoms are not coordinated to the metal centre. The two Ni– S bond lengths, 2.1548(6) and 2.1668(6) Å, are very similar, as are the corresponding S–C distances, 1.704(2) and 1.725(2) Å, and the ligand bite-angle is 97.04(2)°. The structure shows that the phosphorus atom is pyramidal [C–P–C angles: 100.44(10), 104.07(11) and 104.34(11)°] and that the phosphorus lone-pair is almost ideally

¹ Crystal data: NiL₂·CH₂Cl₂: C₃₃H₃₄Cl₂N₄NiP₂S₄, $M_r = 806.43$, monoclinic, space group C2/c, a = 13.9946(18), b = 9.0639(7), c = 29.079(3) Å, $\beta = 97.666(10)^\circ$, U = 3655.5(7) Å³, Z = 4, $D_c = 1.465$ g cm⁻³, $\mu = 1.023$ mm⁻¹, F(000) = 1664. Crystal dimensions $0.20 \times 0.15 \times 0.10$ mm³. Data for NiL₂·CH₂Cl₂ were collected at 150(2) K employing a wavelength of 0.71073 Å, on a Stoe IPDS II image plate diffractometer with $\theta_{\min} = 2.68^\circ$ and $\theta_{\max} = 34.81^\circ$ (index ranges $-21 \le h \le 22$, $-14 \le k \le 14$, $-45 \le l \le 46$). A solution was provided via direct methods and refined by full-matrix least-squares on F^2 using SHELXL-97 [6]. 23,334 reflections were measured, producing 7861 unique data $[I > 2\sigma(I)]$ with $R_{int} = 0.0740$. 213 parameters with no restraints refined to $R_1 = 0.0492$ and $wR_2 = 0.1150$ $[I > 2\sigma(I)]$ with S = 0.857 and residual electron density extremes of 0.938 and -1.149eÅ⁻³. See also supplementary material.

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	Isomer I (and/or II)	Isomer III	Isomer IV	
Ratio ¹ H NMR	26%	13%	61%	
Methyl	δ 3.26 (br s)	δ 3.35 (s)	δ 3.38(s)	
		δ 3.22 (s)	δ 3.31 (s)	
	δ 2.64 (br s)	δ 2.79 (s)	δ 2.83 (s)	
		δ 2.72 (s)	δ 2.69 (s)	
ortho-CH	_	δ 7.95 (m)	δ 7.79 (m)	
(Bound P)				
³¹ P NMR				
(Bound P)	_	$\delta - 20.74$ (d, ${}^{4}J_{\text{PP}(trans)} = 14$ Hz)	δ -21.63 (s)	
(Unbound P)	δ 20.48 (s) or 21.95 (s)	δ 24.72 (d, ${}^{4}J_{PP(trans)} = 14$ Hz)	δ 20.48 (s) or 21.95 (s)	

Table 1 Summary of characteristic ¹H and ³¹P NMR data for isomers I (and/or II), III and IV in CDCl₃ solution

orientated to conjugate into the ligand backbone. However, the relative weakness of this interaction (compared with the dimethylamino group) is demonstrated by the perfect planarity of N(1) [sum of angles = $360.0(2)^\circ$] and the clear short-long-short alternation of bond distances for the chain of atoms N(1)–C(2)–N(2)–C(1): 1.333(3), 1.358(3) and 1.298(3) Å respectively. Moreover, the P(1)– C(1) bond, 1.858(2) Å, is significantly longer than the P(1)–C(phenyl) bonds, 1.826(2) and 1.831(2) Å.

In chloroform solution NiL₂ exists as an equilibrium mixture of three detectable components I (and/or II), III and IV in the approximate ratio 2:1:5 by ¹H and ³¹P NMR spectroscopy (Table 1). These isomers arise due to the ambidentate nature of the ligand, i.e., it may bind as either an (S,S)- or (P,S)-chelate, which combined with cis and trans isomerisation, results in the possibility of six plausible mononuclear structures (Fig. 2). Two of the solution species are readily identified as III and IV as they have C_1 symmetry, as evinced by the observation of four methyl signals in the ¹H NMR spectrum for each ², and the relative integrations of these two sets of signals show they exist in the approximate ratio 1:5. Furthermore, for each of these isomers the ¹H NMR signal for the ortho-CH proton of the single phosphine group bound to the nickel(II) centre is shifted to higher δ^{3} clear of the overlapped multiplet in the range δ 7.28– 7.58 for all the other aryl-CH protons, and these have the correct relative integrations (and are in the ratio 1:5) for the assignment as III and IV. The ³¹P NMR spectrum is also consistent with these assignments, but additionally allows III to be identified as the minor component due to the presence of ³¹P-³¹P coupling, which would only be expected to be large enough to be



Fig. 2. The relevant possible isomers for NiL₂.

observed for the mutually *trans* disposition of the phosphines in III (${}^{4}J_{PP(trans)} = 14$ Hz). In the third observed isomer of NiL₂ the two ligands are equivalent and there is no NMR evidence for the phosphorus atoms being coordinated to the nickel(II) centre, hence this should correspond to the structurally characterised isomer (isomer I). However, the broadness of the two methyl signals in the ¹H NMR spectrum (of which the high δ signal is broader) ⁴ may indicate that both the *trans* (I) and *cis* (II) isomers are present, but interconvert sufficiently quickly on the NMR timescale to appear as a single species. The absence of significant amounts of isomers V and VI may be simply rationalised by the greater *trans*-influence of phosphine ligands favouring III over V, and steric hindrance favouring IV over VI.

In conclusion, the phosphine-containing dithiobiuret analogue 3-diphenylphosphane-carbothioyl-1,1-dimeth-

² There is substantial N–C double bond character in the thioamide group and the energy barrier to rotation is slightly higher ($\Delta G^{t} \sim 100 \text{ kJ mol}^{-1}$) than for the corresponding amides [5], hence inequivalent methyl groups.

³ The assignment of these two high δ signals as *ortho*-protons on the phenyl rings was confirmed by successful computer simulation with reasonable values for the coupling constants: ${}^{2}J_{PH} = 11.8$, ${}^{3}J_{HH} = 8.2$, ${}^{4}J_{HH} \sim 1$ Hz.

⁴ The two broad signals are not coalescing with one another, hence the broadness is probably produced by interconversion of I and II on the NMR timescale. The methyl signals with $\delta > 3.2$ are tentatively assigned to be proximal to sulphur, and those with $\delta < 2.9$ proximal to nitrogen, and this is consistent with the greater broadness of the signal at δ 3.26 being caused by isomer interconversion.

yl-thiourea (HL) has been successfully prepared, and isolated as the nickel(II) complex NiL_2 . Although in the solid state the ligand is coordinated to the nickel(II) ion in a traditional dithiobiuret manner, in solution the ambidentate nature of the ligand becomes apparent. In chloroform the complex exists as a mixture of three isomers, with the major isomer having one phosphine group bound to the nickel centre.

Supplementary material

Supplementary data for is available from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, quoting the deposition number: CCDC 217270.

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