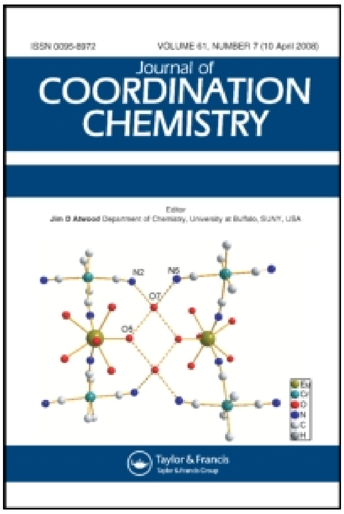

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Condensation of $SCH_2CH_2S^{2-}$ During the Formation of a Nickel(II) Complex Containing Mixed Ligands. Synthesis and Crystal Structure of $Ni(PPh_3)(tpdt)$

Rong Cao[a]; Xinjian Lei[a]; Zhiying Huang[a]; Maochun Hong[a]; Hanqin Liu[a]
[a] Fuzhou Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fujian, China

To cite this Article Cao, Rong , Lei, Xinjian , Huang, Zhiying , Hong, Maochun and Liu, Hanqin(1992) 'Condensation of $SCH_2CH_2S^{2-}$ During the Formation of a Nickel(II) Complex Containing Mixed Ligands. Synthesis and Crystal Structure of $Ni(PPh_3)(tpdt)$', Journal of Coordination Chemistry, 25: 2, 165 — 169

To link to this Article: DOI: 10.1080/00958979209409748

URL: http://dx.doi.org/10.1080/00958979209409748

J. Coord. Chem. 1992, Vol. 25, pp. 165–169
Reprints available directly from the publisher
Photocopying permitted by license only

CONDENSATION OF $SCH_2CH_2S^{2-}$ DURING THE FORMATION OF A NICKEL(II) COMPLEX CONTAINING MIXED LIGANDS. SYNTHESIS AND CRYSTAL STRUCTURE OF $Ni(PPh_3)(tpdt)$

RONG CAO,* XINJIAN LEI, ZHIYING HUANG, MAOCHUN HONG
and HANQIN LIU

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

(Received May 10, 1991; in final form July 17, 1991)

Reaction of $NiCl_2$, PPh_3 and Na_2edt ($edt^{2-} = SCH_2CH_2S^{2-}$) in methanol gives rise to the cleavage of the C–S bond in edt and a new nickel(II) complex, $Ni(PPh_3)(tpdt)$ ($tpdt^{2-} = SCH_2CH_2SCH_2CH_2S^{2-}$). The complex crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.383(4)$, $b = 16.380(4)$, $c = 14.177(4)$ Å, $\beta = 102.75(3)°$, $V = 2125.2$ Å^3, $Z = 4$; $M_r = 473.30$; $D_c = 1.479$ gcm^{-3}; $F(000) = 984$; $\mu = 12.79$ cm^{-1}. Final R is 0.052 for 2017 observed reflections. The nickel atom is four-coordinated with a distorted square-planar geometry with Ni–S distances in the range 2.150–2.180 Å and with Ni–P equal to 2.187 Å.

Keywords: Nickel, condensation, crystal structure, 1,2-ethanedithiol, phosphine

INTRODUCTION

Because of their geometric and electronic structural features, and potential uses as catalysts,[1,2] metal complexes containing sulfur and phosphine ligands have been studied extensively.[3] The mechanism of the hydrodesulfurization process is also of interest for many inorganic chemists. Transition metals such as Co, Ni and Nb play an important role in the hydrodesulfurization catalysis. Recently, a series of transition metal complexes containing mixed phosphine and thiolate ligands, including $(Et_4N)Co(SPh)_3(PPh_3)$,[4] $Co(SPh)_2L$ ($L = Ph_2P(CH_2)_3PPh_2$, $Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2$),[5] $Co_2(dppx)(SPh)_4$ ($dppx = Ph_2PCH_2PPh_2$, $Ph_2PCH_2CH_2PPh_2$),[6,7,8] $Co_3(SC_6H_4S)_3(PBu^n{}_3)_3$,[9] and $Ni(SR)_2(PBu^n{}_3)_2$ (R = Ph, *p*-tol),[10,11] have been synthesized in our laboratory. By reaction of $NiCl_2$, Na_2edt and PPh_3 in MeOH, we obtained two nickel(II) complexes, $Ni(PPh_3)(tpdt)$ and $[Ni(PPh_3)(edt)]_2$. Herein, the synthesis and X-ray crystal structure of $Ni(PPh_3)(tpdt)$ is reported.

EXPERIMENTAL

Preparation of the complex

To a solution of PPh_3 (1.56 g, 6 mmol) and Na_2edt (0.42 g, 3 mmol) in 35 cm^3 of deoxygenated MeOH, was added solid anhydrous $NiCl_2$ (0.42 g, 3 mmol). After

---

[*] Author for correspondence.

stirring for 24 h, the brown precipitate formed was filtered and the filtrate kept at 4°C for several days to yield brown-red platy crystals (20%). Anal.: Calcd. for $C_{22}H_{23}NiPS_3$: C, 55.82; H, 4.89%. Found: C, 55.88; H, 4.82%. IR (KBr): 390(m), 440(m), 498(s), 508(s), 529(s) cm^{-1}.

Intensity data collection and structure determination

A crystal of dimensions 0.10 × 0.20 × 0.30 mm was mounted on a RIGAKU AFC5R four circle diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.71069$ Å). The parameters used in intensity collection and refinement together with crystal data are summarized in Table I.

TABLE I

Crystal data, intensity collection and structure refinement parameters for $Ni(PPh_3)(tpdt)$.

Formula	$NiS_3PC_{22}H_{23}$
M_r	473.30
Dimensions, mm	0.1 × 0.2 × 0.3
Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	9.383(4)
b, Å	16.380(4)
c, Å	14.177(4)
β, deg	102.75(3)
V, $Å^3$	2125.2
Z	4
D_c, g/cm^3	1.479
Scan range, deg	$2 < 2\theta < 50$
Scan mode	ω–2θ
Total reflections	4638
Unique reflections ($I > 3\sigma(I)$)	2017
$F(000)$	984
μ, cm^{-1}	12.79
R[a]	0.052
R_w[b]	0.066

[a] $R = (\Sigma||F_o| - |F_c||/\Sigma|F_o|)$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = [\sigma^2(F_o) + (0.001|F_o|)^2 + 1.0]$.

All calculations were performed on a VAX 11/785 computer with the SDP program package. Intensity data were corrected for Lp factors and empirical absorptions; 2017 reflections with $I > 3\sigma$ (I) were used for the structure determination and refinement. The structure was solved by direct methods and difference Fourier syntheses to locate all non-hydrogen atoms and refined by full-matrix least-squares methods with anisotropic temperature factors for all non-hydrogen atoms. The final values of R and R_w are also given in Table I.

Physical measurements

I.r. spectra were recorded on a Perkin Elmer 577 spectrometer in KBr pellets. ^1H NMR spectra were recorded on a Varian FT-80A spectrometer with TMS as internal standard.

TABLE II
Positional parameters and estimated standard deviations for $Ni(PPh_3)(tpdt)$.

Atom	x/a	y/b	z/c	$B(Å^2)$
Ni	0.9019(1)	0.06679(6)	0.65763(7)	2.51(2)
S(1)	0.7664(3)	0.1479(1)	0.5545(2)	4.27(6)
S(2)	0.7763(2)	−0.0347(1)	0.5876(2)	3.19(4)
S(3)	1.0693(2)	−0.0185(1)	0.7295(2)	3.34(5)
P	0.9966(2)	0.1654(1)	0.7556(1)	2.29(4)
C(11)	0.644(1)	0.0806(6)	0.4702(7)	4.8(2)
C(12)	0.714(1)	−0.0006(6)	0.4642(6)	4.4(2)
C(13)	0.9127(9)	−0.1118(5)	0.5798(7)	4.3(2)
C(14)	1.004(1)	−0.1190(5)	0.6805(7)	4.4(2)
C(211)	0.9339(7)	0.1621(5)	0.8680(5)	2.4(2)
C(212)	0.9265(9)	0.2322(5)	0.9207(6)	3.7(2)
C(213)	0.887(1)	0.2281(6)	1.0108(6)	4.4(2)
C(214)	0.8563(9)	0.1523(6)	1.0474(6)	4.1(2)
C(215)	0.8615(9)	0.0812(6)	0.9937(6)	4.0(2)
C(216)	0.9012(8)	0.0858(5)	0.9039(6)	3.3(2)
C(221)	1.1951(8)	0.1617(4)	0.7941(5)	2.5(2)
C(222)	1.2662(9)	0.1724(5)	0.8907(6)	3.6(2)
C(223)	1.4206(9)	0.1705(6)	0.9158(7)	4.4(2)
C(224)	1.5032(9)	0.1593(5)	0.8462(6)	3.7(2)
C(225)	1.4294(9)	0.1498(5)	0.7492(6)	3.6(2)
C(226)	1.2769(8)	0.1505(5)	0.7240(6)	2.9(2)
C(231)	0.9584(8)	0.2713(4)	0.7160(5)	2.6(2)
C(232)	1.0730(9)	0.3242(5)	0.7098(6)	3.2(2)
C(233)	1.040(1)	0.4058(5)	0.6807(7)	4.1(2)
C(234)	0.8972(9)	0.4341(5)	0.6606(7)	4.3(2)
C(235)	0.786(1)	0.3784(6)	0.6664(7)	4.6(2)
C(236)	0.8158(8)	0.2977(5)	0.6955(6)	3.5(2)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) \times [a^2 \times \beta(1,1) + b^2 \times \beta(2,2) + c^2 \times \beta(3,3) + ab(\cos\gamma) \times \beta(1,2) + ac(\cos\beta) \times \beta(1,3) + bc(\cos\alpha) \times \beta(2,3)]$.

RESULTS AND DISCUSSION

The title complex was obtained from the reaction of $NiCl_2$ with Na_2edt and PPh_3 in a 1:1:2 molar ratio by using standard Schlenck techniques in MeOH. It is interesting to note that although edt was used as initial reactant, the complex obtained contains tpdt instead of edt, indicating a condensation of two edt ligands and involving a cleavage of the C–S bond. According to the literature,[12] the H^+ ion is important in the disruption of C–S during the formation of the complex NbS(edt)(tpdt). In our reaction, two complexes, $Ni(PPh_3)(tpdt)$ (**I**; 20%) and $[Ni(PPh_3)(edt)]_2$ (**II**; 20%), were obtained simultaneously; the former remained in the reaction solution and the latter formed a precipitate. Complex (**I**) can also be obtained in air when EtOH is used as solvent. However, **I** has not been obtained if the reaction was carried out in non-protic solvents such as CH_3CN; in the same medium, if the reaction was carried out without PPh_3, $Ni_2(edt)_3^{2-}$ or $Ni_3(edt)_4^{2-}$ was obtained and no cleavage of the C–S bond occurred.[13,14,15] It could be said that any one of the constituents, Ni(II), PPh_3 or H^+, plays an important role in the disruption of the C–S bond. In the light of our results, we propose that attack of H^+ or ROH on edt in the presence of Ni(II) and PPh_3, followed by cleavage of the C–S bond and subsequent condensation of edt ligands, leads to the formation of I. Further research on the reaction mechanism is under way.

Atomic coordinates and thermal parameters for the title complex are given in Table II. Selected bond lengths and bond angles are listed in Table III.

TABLE III
Selected bond lengths (Å) and bond angles (deg) for $Ni(PPh_3)(tpdt)$.

		Bond lengths	
Ni-S(1)	2.168(2)	S(2)-C(13)	1.817(7)
Ni-S(2)	2.150(2)	S(3)-C(14)	1.843(7)
Ni-S(3)	2.180(2)	P-C(211)	1.820(6)
Ni-P	2.187(2)	P-C(221)	1.824(6)
S(1)-C(11)	1.837(7)	P-C(231)	1.835(6)
S(2)-C(12)	1.804(6)		
		Bond angles	
S(1)-Ni-S(2)	88.99(7)	Ni-S(2)-C(12)	103.8(3)
S(1)-Ni-S(3)	164.41(8)	Ni-S(2)-C(13)	104.1(2)
S(2)-Ni-S(3)	89.14(7)	Ni-S(3)-C(14)	104.5(2)
S(1)-Ni-P	94.07(8)	C(12)-S(2)-C(13)	103.3(4)
S(2)-Ni-P	165.67(7)	Ni-P-C(211)	111.7(2)
S(3)-Ni-P	91.55(7)	Ni-P-C(221)	114.3(2)
Ni-S(1)-C(11)	105.0(2)	Ni-P-C(231)	118.7(2)

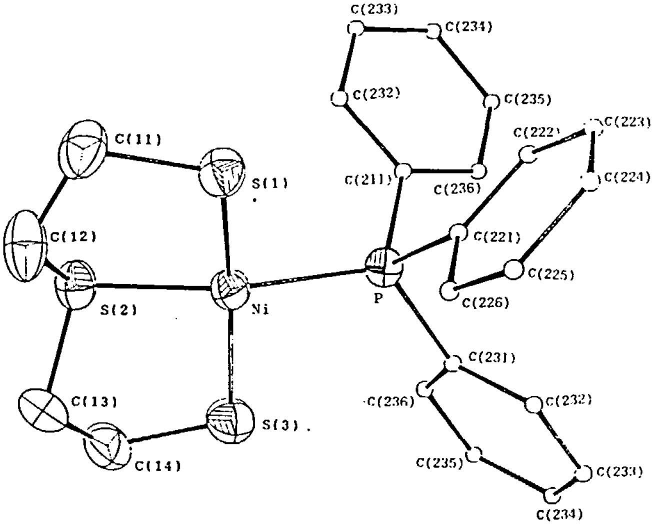

FIGURE 1 Molecular structure of the title complex.

Figure I depicts the molecular structure of the title complex. The Ni atom is surrounded by three sulphur and one phosphorus atoms in a distorted square-planar geometry. The average Ni–S bond length (2.166 Å) is shorter than those found in nickel complexes containing monodentate thiolate and phosphine ligands such as Ni(S-*p*-tol)$_2$(PBu$^n{}_3$)$_2$ (2.219 Å)[10] and Ni(SPh)$_2$(PBu$^n{}_3$)$_2$,[11] but approximately the same as those in Ni$_2$(tpdt)$_2$[16] and in nickel(II) complexes with dithiolate ligands.[13,14,15] The thiolato sulfur–Ni bonds (2.168, 2.180 Å) are longer than thioether sulfur–Ni bond (2.150 Å), and the thiolato sulfur–C bonds (1.837, 1.843 Å) are also longer than thioether sulfur–C bonds (1.804, 1.817 Å). The Ni–P (2.180 Å) bond is shorter than those found in Ni(S-*p*-tol)$_2$(PBu$^n{}_3$)$_2$ (2.237 Å) and Ni(SPh)$_2$(P-Bu$^n{}_3$)$_2$ (2.245 Å), but very similar to those in others (2.166–2.205 Å).[17]

The complex is diamagnetic. Its ^{1}H NMR spectrum in DMSO-d_6 shows two peaks at 2.52 and 3.27 ppm for the tpdt ligand (similar to the complex NbS(edt)(tpdt)[12]) and one broad peak at 7.37 ppm for the PPh$_3$ ligand.

ACKNOWLEDGEMENTS

We acknowledge support from the Chinese National Natural Science Foundation and the assistance of Mr. Daxu Wu with ^{1}H NMR experiments.

SUPPLEMENTARY MATERIAL

Complete lists of thermal parameters, bond distances, bond angles and observed and calculated structure factors have been deposited with the Editor and are available upon request.

REFERENCES

1. H. Topsoe and B.S. Clause, *Catal. Rev.*, **22**, 395 (1984).
2. B. Bodanovic, P. Gottsch and M. Rubach, *J. Mol. Catal.*, **11**, 135 (1981).
3. D. Fenske, J. Ohmer, J. Hachgenei and K. Merzweiter, *Angew. Chem., Int. Ed. Engl.*, **27**, 1277 (1988), and refs therein.
4. F.L. Jiang, G.W. Wei, X.J. Lei, Z.Y. Huang, M.C. Hong and H.Q. Liu, *J. Coord. Chem.*, in press.
5. G.W. Wei, M.C. Hong, Z.Y. Huang and H.Q. Liu, *J. Chem. Soc., Dalton Trans.*, in press.
6. G.W. Wei, H.Q. Liu, Z.Y. Huang, M.C. Hong, L.R. Huang and B.S. Kang, *Polyhedron.*, **10**, 553 (1991).
7. G.W. Wei and H.Q. Liu, *Acta Cryst.*, in press.
8. G.W. Wei, H.Q. Liu, Z.Y. Huang, L.R. Huang and B.S. Kang, *J. Chem. Soc., Chem. Commun.*, 1939 (1989).
9. B.S. Kang, J.H. Peng, M.C. Hong, D.X. Wu, X.T. Chen, L.H. Weng, X.J. Lei and H.Q. Liu, *J. Chem. Soc., Dalton Trans.*, in press.
10. F.L. Jiang, G.W. Wei, X.J. Lei, Z.Y. Huang, M.C. Hong and H.Q. Liu, submitted for publication.
11. R. Cao, unpublished results.
12. K. Tatsumi, Y. Sekiguchi and A. Nakamura, *J. Am. Chem. Soc.*, **108**, 1358 (1986).
13. J.R. Nicholson, G. Christon, J.C. Huffman and K. Folting, *Polyhedron*, **6**, 863 (1987).
14. B.S. Snyder, C.P. Rao and R.H. Holm, *Aust. J. Chem.*, **39**, 963 (1986).
15. W. Tremel, M. Kriege, B. Krebs and G. Henkel, *Inorg. Chem.*, **27**, 3886 (1988).
16. G.A. Barclay, E.M. McPartlin and N.C. Stephenson, *Inorg. Nucl. Chem. Lett.*, **3**, 397 (1967).
17. M.C. Hong, Z.Y. Huang and H.Q. Liu, *J. Chem. Soc., Chem. Commun.*, 1210 (1990).