Pergamon

0277–5387(94)00361–0

Polyhedron Vol. 14, No. 8, pp. 991–996, 1995

0277–5387/95 $9.50+0.00

NICKEL COMPLEXES WITH SULPHUR AND NITROGEN DONOR LIGANDS, CRYSTAL AND MOLECULAR STRUCTURE OF $[(PPh_3)_2Cu(DTA)Ni(DTA)Cu(PPh_3)_2]$ (H_2DTA = DITHIOOXAMIDE)

PAVEL KOPEL,* FRANTIŠEK BŘEZINA, ZDENĚK TRÁVNÍČEK, ZDENĚK ŠINDELÁŘ and JAN LASOVSKÝ

Department of Inorganic Chemistry, Palacký University, Křížkovského 10,
771 47 Olomouc, Czech Republic

and

JAROMÍR MAREK

Department of Inorganic Chemistry, Masaryk University, Kotlářská 10,
661 37 Brno, Czech Republic

(*Received* 18 *July* 1994; *accepted* 31 *August* 1994)

Abstract—The complexes $[Ni(bipy)(DTA)(H_2O)_2]\cdot H_2O$, $[Ni(dtc)(HDTA)]\cdot H_2O$, $[Ni(phen)(ATF)_2]\cdot 5H_2O$ and $[Ni(phen)(dtc)_2]$ (bipy = 2,2′-bipyridine, H_2DTA = dithiooxamide, Hdtc = diethyldithiocarbamate, phen = 1,10-phenanthroline, HATF = 2-aminothiophenol) have been prepared. Their magnetochemical and spectral properties are discussed. Some of the complexes have been studied by cyclic voltammetry. The X-ray crystal structure of $[(PPh_3)_2Cu(DTA)Ni(DTA)Cu(PPh_3)_2]$, where PPh_3 = triphenylphosphine, was determined. The sulphur atoms of dithiooxamides are coordinated to copper atoms, while nitrogen atoms form a square planar surrounding nickel. The copper atoms are in an approximately tetrahedral environment.

It was found that nickel plays an important role in biological systems.[1] Nickel EXAFS studies of some hydrogenases indicate that the nickel centre is surrounded by sulphur, nitrogen and/or oxygen atoms.[2] Nickel complexes with such combinations of ligands can serve not only as models for some biological systems, but also can stabilize less usual oxidation states of nickel. The complexes of nickel with dithiocarbamates and aminothiophenol are well known.[3] The complexes of dithiooxamide have been used in analytical chemistry for a long time.[4] Their industrial applications as metal deactivators in petroleum products, as vulcanization accelerators and as colour sources in duplicating processes are known. They can also be used for inhibition of certain bacteria and dehydrogenases and also as reagents in certain syntheses.[5,6] In neutral or basic solutions dithiooxamide forms, with metal cations, polymeric complexes of unknown structure. Complexes of the formula $M(H_2DTA)X_{2-4}$ are formed in strong acid solutions.[7–9] An X-ray study of dithiooxamide showed the *trans* conformation of sulphur and nitrogen atoms.[10,11] X-ray crystal structures of some nitrogen derivatives of dithiooxamide have been solved.[12–15] These molecules also contain the *trans* configuration of the dithiooxamide derivatives. In our work we were looking for combinations of ligands suitable for stabilization of nickel in higher oxidation states. The other aim was to prepare a single crystal of a nickel–dithiooxamide complex for an X-ray study.

---

*Author to whom correspondence should be addressed.

EXPERIMENTAL

$Ni(bipy)_2Cl_2 \cdot 6H_2O$, $Ni(phen)_2Cl_2 \cdot 5H_2O$ and $Cu(PPh_3)_3I$ were prepared according to literature methods.[16,17] Other chemicals were used as received.

IR spectra were recorded on a Specord IR 75 instrument using Nujol mulls and the electronic spectra were recorded on a Specord M 40 spectrometer (Carl Zeiss, Jena). Magnetic susceptibilities of polycrystalline samples were measured by the Faraday method using a Sartorius M-25D electrobalance. The calibrant employed was $Co[Hg(SCN)_4]$, for which the magnetic susceptibility was taken as 16.44×10^{-6} cm^3 g^{-1}. The correction for diamagnetism of the constituent atoms was calculated by use of Pascal's constants. The magnetism of the samples was found to be field independent.

Thermal decomposition was studied with a Q 1500 D Derivatograph (MOM Budapest) with a sample weight of 100–120 mg and temperature increase of 2.5°C min^{-1}. The cyclic voltammograms were measured on a Princeton Applied Research Model 273 EG and G potentiostat/galvanostat in the three-electrode arrangement. A glassy carbon (gC) working electrode with an area of 0.08 cm^2 and porosity of 1–3% was used. The reference electrode was a saturated calomel electrode (SCE) and the auxiliary electrode was made of platinum foil with a large surface area. The potential scan rate was in the range 0.005–0.5 Vs^{-1}. All potential values are related to the SCE.

The X-ray structure determination was performed on a KUMA KM-4 diffractometer.

Crystals of $[(PPh_3)_2Cu(DTA)Ni(DTA)Cu(PPh_3)_2]$ were obtained from a mixture of $(Me)_2CO$, $CHCl_3$ and MeOH (1 : 1 : 1). The dimensions of the crystal used for data collection were $0.80 \times 0.50 \times 0.20$ mm. Final values of the lattice parameters were determined from 25 reflections in the range $19° < 2\theta < 23°$. Diffraction intensities were measured at 291 K within the $4° < 2\theta < 50°$ region with ω-2θ scan techniques using graphite monochromated Mo-K_α radiation, $\lambda = 0.71073$ Å. Index ranges: $-14 \leqslant h \leqslant 0$, $0 \leqslant k \leqslant 23$, $-17 \leqslant l \leqslant 17$. The crystal stability during the data collection was checked by measuring three standard reflections (−5 5 2, 0 −1 7, 1 1 1) after every 300 measurements; no significant change of their intensities was detected. Extinction and absorption corrections were not applied. The structure was solved by the heavy-atom method. All atoms, except hydrogens, were refined anisotropically by the full-matrix least-squares procedure with weight $w = 1/[\sigma^2(F_0^2)+(0.12P)^2+7.0P]$, where $P = (F_0^2+2F_c^2)/3$. The hydrogen atoms were positioned theoretically. The maximum and minimum electron densities on the final differential Fourier map were 0.923 and −0.649 e $Å^{-3}$. The calculations were performed using the SHELXS-86 and SHELXL-93 programmes, and pictures were drawn by ORTEP.[18]

Preparation of $[Ni(bipy)(DTA)(H_2O)_2] \cdot H_2O$

To a solution of $Ni(bipy)_2Cl_2 \cdot 6H_2O$ (1.95 mmol) in EtOH was added a solution of dithiooxamide (1.80 mmol). To the red–violet solution 1.92 mmol of Et_3N was added dropwise. The red precipitate was filtered off, washed with EtOH and Et_2O and dried in a vacuum desiccator over KOH.

Preparation of $[Ni(dtc)(HDTA)] \cdot H_2O$

Nadtc (2.10 mmol) and H_2DTA (2.08 mmol) were dissolved in EtOH. This solution was added to a solution of $NiCl_2 \cdot 6H_2O$ (2.11 mmol) in the same solvent. The reaction mixture was stirred and refluxed for 1 h. The resulting brown precipitate was filtered off and a violet solution was left for crystallization. From the solution violet microcrystals were formed and analysed.

Preparation of $[Ni(phen)(ATF)_2] \cdot 5H_2O$

A solution of 1.3 mmol of $[Ni(phen)_2]Cl_2 \cdot 5H_2O$ in 15 cm^3 of MeOH was added to a stirred solution of 2.5 mmol of HATF and 2.5 mmol of NEt_3 in 10 cm^3 of MeOH. After 3 h of stirring a green precipitate was collected by filtration and washed with MeOH.

Preparation of $[Ni(phen)(dtc)_2]$

KOH (2.14 mmol) in 5 cm^3 of water, 1.94 mmol of Et_2NH and 1.98 mmol of CS_2 were stirred for 30 min at room temperature. This solution was then added to a solution of 0.95 mmol of $Ni(phen)_2Cl_2 \cdot 5H_2O$ in 10 cm^3 of water. The resulting brown–red precipitate was washed with water.

Preparation of $[(PPh_3)_2Cu(DTA)Ni(DTA)Cu(PPh_3)_2]$

To a stirred solution of $Cu(PPh_3)_3I$ (1.02 mmol) in $CHCl_3$ was added H_2DTA (1.00 mmol) in Me_2CO and Et_3N (1.94 mmol). After stirring for a few minutes a solution of $Ni(phen)_2Cl_2 \cdot 5H_2O$ (0.98 mmol) in MeOH was added. The resulting red solution was then stirred for 1 h and left for 5 days, until red crystals formed. They were filtered off, washed with a small amount of Me_2CO–$CHCl_3$

(1 : 1) and dried. Found: C, 61.4; H, 4.6; N, 4.5. Calc. for $C_{76}H_{64}Cu_2NiP_4S_4$: C, 62.0; H, 4.4; N, 3.8%.

RESULTS AND DISCUSSION

The chemical compositions of the compounds, together with some physical properties, are given in Table 1.

The magnetic moments of these nickel(II) complexes, except for [Ni(dtc)(HDTA)] · H_2O, have values characteristic for octahedral coordination. Their magnetic moments vary in the range of 2.57–3.17 B.M. The assignment of octahedral geometries is also supported by the electronic absorption spectra, in which sets of *d–d* bands are observed at 26,000–29,000 cm^{-1} [$^3A_{2}g \rightarrow {}^3T_{1}g(P)$] and 17,000–20,500 cm^{-1} [$^3A_{2}g \rightarrow {}^3T_{1}g(F)$]. The third transitions to the $^3T_{2}g$ were not observed.

[Ni(dtc)(HDTA)]·H_2O is diamagnetic, with only one observed absorption maximum (in the visible region) near 19,200 cm^{-1}, probably corresponding to the $^1A_{1}g \rightarrow {}^1A_{2}g$ transition.[19] This is why we suggest square planar geometry for the above mentioned complex. In the IR spectra we have only assigned ν(CN) and ν(CS) vibrations (see Table 2).[20–22]

Dehydrations of [Ni(dtc)(HDTA)]·H_2O and [Ni(phen)(ATF)$_2$]·$5H_2O$ were found by TGA curves at 70°C and 50°C, respectively. In the thermal study of [Ni(bipy)(DTA)(H_2O)$_2$]·H_2O heating above 60°C led to the loss of one water molecule and further mass loss expected for the remaining water molecules occurred at 140°C.

The electrochemical studies show that [Ni(phen)(ATF)$_2$]·$5H_2O$, [Ni(phen)(dtc)$_2$] and [Ni(dtc)(HDTA)]·H_2O undergo anodic oxidation in 5×10^{-4} mol dm^{-3} solutions in DMF. The linear dependence of the height of the anodic peaks on the concentration and on the square root of the potential scan rate indicate that the anodic oxidation is diffusion-controlled and the values of the peak height approach those for a one-electron irreversible process in the case of [Ni(phen)(ATF)$_2$]·$5H_2O$ and [Ni(phen)(dtc)$_2$] and a two-electron irreversible process for [Ni(dtc)(HDTA)]·H_2O. [Ni(bipy)(DTA)(H_2O)$_2$]·H_2O was not electrochemically studied due to its low solubility. Comparing phenanthroline complexes, we note that the diethyldithiocarbamate derivative

Table 1. Analytical data and physical properties of the complexes

Compound	Found (calc.), %				μ_{eff}(B.M.) (290 K)	E_{pa} (mV)
	Ni	C	H	N		
[Ni(bipy)(DTA)(H_2O)$_2$]·H_2O	15.6 (15.2)	36.9 (37.2)	3.6 (4.2)	14.3 (14.5)	2.57	
[Ni(dtc)(HDTA)]·H_2O	17.6 (17.1)	23.7 (24.4)	3.6 (4.4)	12.1 (12.2)	dia	670
[Ni(phen)(ATF)$_2$]·$5H_2O$	9.7 (10.2)	50.1 (50.0)	3.7 (3.5)	9.7 (9.7)	2.58	710
[Ni(phen)(dtc)$_2$]	10.3 (11.0)	50.3 (49.3)	5.0 (5.3)	10.5 (10.5)	3.17	620

Table 2. UV–vis and IR data

Compound	ν (cm^{-1})	Transition	ν(CN)	ν(CS)
[Ni(bipy)(DTA)(H_2O)$_2$]·H_2O	32,500	CT[a]	1440 s	852 m
	26,000	$^3A_{2}g \rightarrow {}^3T_{1}g(P)$	1596 m	900 w
	17,000	$^3A_{2}g \rightarrow {}^3T_{1}g(F)$		950 w
[Ni(dtc)(HDTA)]·H_2O	32,100	CT	1444 s	840 w
	19,200	$^1A_{1}g \rightarrow {}^1A_{2}g$	1540 w	904 m
[Ni(phen)(ATF)$_2$]·$5H_2O$	33,300	CT	1512 s	856 m
	29,000	$^3A_{2}g \rightarrow {}^3T_{1}g(P)$	1576 m	932 w
	20,000	$^3A_{2}g \rightarrow {}^3T_{1}g(F)$		960 w
[Ni(phen)(dtc)$_2$]	33,800	CT	1444 s	844 s
	28,800	$^3A_{2}g \rightarrow {}^3T_{1}g(P)$	1584 w	912 w
	20,500	$^3A_{2}g \rightarrow {}^3T_{1}g(F)$		984 m

[a] Charge transfer.

Table 3. Crystal data and structural refinement for $[(PPh_3)_2Cu(DTA)Ni(DTA)Cu(PPh_3)_2]$

Empirical formula	$C_{38}H_{32}Cu_1N_2Ni_{0.5}P_2S_2$
Formula weight	735.61
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 11.826(2)$ Å
	$b = 19.933(5)$ Å
	$c = 15.163(3)$ Å
	$\beta = 105.51(2)^\circ$
Volume	3444.2(12) A^3
Z	4
Density (calculated)	1.419 mg m^{-3}
Absorption coefficient	1.143 mm^{-1}
$F(000)$	1516
Reflections collected	6314
Independent reflections	6002($R_{\rm int}$ = 0.0279)
Data/restraints/parameters	6002/0/419
$S_{\rm obs/total}$	0.989/0.878
$R_{\rm obs}[I > 2\sigma(I)]$	$R = 0.0573$, $R_w = 0.1661$
$R_{\rm total}$	$R = 0.1124$, $R_w = 0.1956$

is oxidized at a lower potential than the aminothiophenol derivative. Chemical oxidation of these complexes failed. Oxidation by I_2, $NOClO_4$ and $Na_2S_2O_8$ led to undefined products only.

Because the nickel complexes studied were either precipitates or microcrystalline substances, we sought another complex suitable for X-ray crystallographic study. We decided upon the preparation of a heteronuclear complex because we wanted to use the bridging properties of dithiooxamide and to prevent formation of polymeric precipitate. We conclude that the affinity of copper atoms to sulphur ligands and the affinity of nickel to nitrogen have lead to the *cis* conformation of the dithiooxamide. The other products of the reaction will be of further interest together with the physical properties of the trinuclear complex.

Molecular structure of $[(PPh_3)_2Cu(DTA)Ni(DTA)Cu(PPh_3)_2]$

Table 3 lists the basic crystallographic data and refinement parameters of the complex. Important bond distances and bond angles are listed in Table 4. The skeleton of the molecule is shown in Fig. 1 and an ORTEP drawing of the discussed part is given in Fig. 2. The molecule is centrosymmetric with the nickel atom on the centre of symmetry. From the structure it is obvious that the bridging dithiooxamide ligands are in the *cis* conformation, which is, for dithiooxamide, rather unusual. Bond lengths and angles as well as zero deviations of the nickel, N(1), N(2), N(1a) and N(2a) atoms from a

Table 4. Important bond lengths (Å) and angles (°) for $[(PPh_3)_2Cu(DTA)Ni(DTA)Cu(PPh_3)_2]$

Cu(1)—P(2)	2.256(2)	P(2)—Cu(1)—P(1)	118.84(6)
Cu(1)—P(1)	2.282(2)	P(2)—Cu(1)—S(1)	114.01(7)
Cu(1)—S(1)	2.351(2)	P(1)—Cu(1)—S(1)	108.09(7)
Cu(1)—S(2)	2.357(2)	P(2)—Cu(1)—S(2)	113.52(7)
Ni—N(1)	2.081(7)	P(1)—Cu(1)—S(2)	108.94(7)
Ni—N(1a)^a	2.081(7)	S(1)—Cu(1)—S(2)	89.53(7)
Ni—N(2)	2.129(6)		
Ni—N(2a)^a	2.129(6)	N(1)—Ni—N(2)	92.2(2)
P(1)—C(51)	1.819(6)	N(1a)^a—Ni—N(2)	87.8(2)
P(1)—C(41)	1.825(6)	N(1)—Ni—N(2a)^a	87.8(2)
P(1)—C(61)	1.834(6)	N(1A)—Ni—N(2a)^a	92.2(2)
P(2)—C(11)	1.817(6)		
P(2)—C(21)	1.838(6)	C(2)—S(1)—Cu(1)	99.6(2)
P(2)—C(31)	1.846(6)	C(1)—S(2)—Cu(1)	99.1(2)
S(1)—C(2)	1.584(7)	C(1)—N(1)—Ni	103.2(5)
S(2)—C(1)	1.609(7)	C(2)—N(2)—Ni	100.4(4)
N(1)—C(1)	1.448(8)	N(1)—C(1)—C(2)	121.4(6)
N(2)—C(2)	1.481(8)	N(1)—C(1)—S(2)	114.2(5)
C(1)—C(2)	1.483(8)	C(2)—C(1)—S(2)	124.4(5)
		N(2)—C(2)—C(1)	122.5(6)
		N(2)—C(2)—S(1)	111.9(5)
		C(1)—C(2)—S(1)	125.6(5)

^{a}Symmetry transformations used to generate equivalent atoms: $-x$, $-y$, $-z+1$.

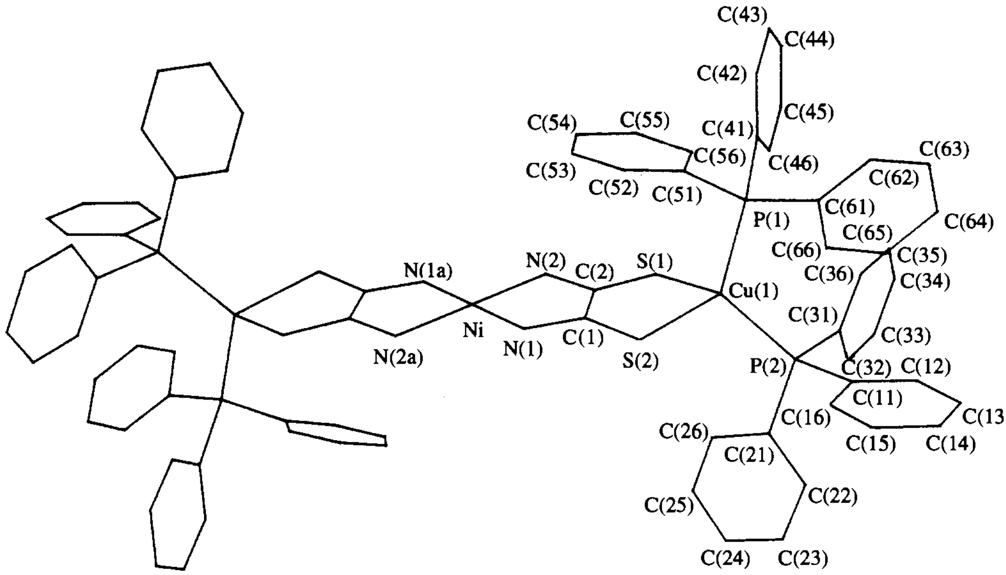

Fig. 1. The skeleton of [(PPh$_3$)$_2$Cu(DTA)Ni(DTA)Cu(PPh$_3$)$_2$].

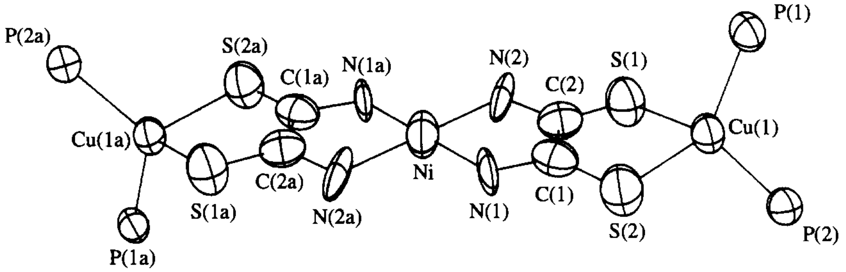

Fig. 2. An ORTEP drawing of the central core of [(PPh$_3$)$_2$Cu(DTA)Ni(DTA)Cu(PPh$_3$)$_2$].

plane show an ideal square-planar arrangement of nitrogen atoms around nickel. The deviation of the copper atoms from this plane is 0.041 Å. The distorted tetrahedral arrangement of the CuS$_2$P$_2$ coordination sphere was proved. The copper atom is coordinated by two sulphur atoms of the bridged dithiooxamide molecule and by two phosphorus atoms from triphenylphosphine molecules.

Supplementary material available. Tables of atomic positional parameters, complete tables of bond distances and bond angles, tables of anisotropic thermal displacement parameters and listings of observed and calculated structure factors.

REFERENCES

1. M. G. Kanatzidis, *Inorg. Chim. Acta* 1990, **168**, 101 and references therein.
2. P. A. Lindahl, N. Kojima, R. P. Hausinger, J. A. Fox, B. K. Teo, C. T. Walsh and W. H. Orme-Johnson, *J. Am. Chem. Soc.* 1984, **106**, 3062.
3. S. J. Lippard, *Prog. Inorg. Chem.* 1970, **11**, 234.
4. P. Ray and J. Xavier, *J. Indian Chem. Soc.* 1961, **38**, 535.
5. M. R. Green, N. Jubran, B. E. Bursten and D. H. Busch, *Inorg. Chem.* 1987, **26**, 2326 and references therein.
6. R. Abdur and C. Z. Hussain, *J. Chem. Soc. Pak.* 1992, **14**, 111.
7. M. Abboudi, A. Mosset and J. Galy, *Inorg. Chem.* 1985, **24**, 2091.
8. G. Peyronel, A. C. Fabretti and G. C. Pellacani, *J. Inorg. Nucl. Chem.* 1973, **35**, 973.
9. P. M. Solozhenkin, A. V. Ivanov and E. V. Rakitina, *Zh. Neorg. Khim.* 1983, **28**, 3081.
10. P. J. Wheatley, *J. Chem. Soc.* 1965, 396.
11. A. Mosset, M. Abboudi and J. Galy, *Z. Crist.* 1983, **164**, 171.
12. J. J. Girerd, S. Jeannin and O. Kahn, *Inorg. Chem.* 1978, **17**, 3034.
13. C. Chauvel, J. J. Girerd, Y. Jeannin, O. Kahn and G. Lavigne, *Inorg. Chem.* 1979, **18**, 3015.
14. R. Veit, J. J. Girerd, O. Kahn, F. Robert, Y. Jeannin and N. E. Murr, *Inorg. Chem.* 1984, **23**, 4448.
15. R. Veit, J. J. Girerd, O. Kahn, F. Robert and Y. Jeannin, *Inorg. Chem.* 1986, **25**, 4175.
16. K.-C. Buschbeck, *Gmelins Handbuch der Anor-*

ganischen Chemie, *Nickel*, Teil C, Lieferung 1, 8th edn. Verlag Chemie, GMBH Weinheim (1968).

17. G. Costa, E. Reisenhofer and L. Stefani, *J. Inorg. Nucl. Chem.* 1965, **27**, 2581.
18. G. M. Sheldrick, SHELXS-86, *Acta Cryst.* 1990, **A46**, 467; G. M. Sheldrick, SHELXL-93, *J. Appl. Cryst.* 1993, in preparation; C. K. Johnson, ORTEP. Report ORNL-3794, Oak Ridge National Laboratory, Tennessee (1971).
19. A. B. P. Lever, *Inorganic Electronic Spectroscopy.* Elsevier, Amsterdam (1968).
20. S. V. Larionov, L. A. Patrina, I. M. Oglezneva and E. M. Uskov, *Koord. Khim.* 1984, **10**, 92.
21. D. M. Vinickii, K. A. Solntsev, N. T. Kuznetsov and L. V. Goeva, *Zh. Neorg. Khim.* 1986, **31**, 2326.
22. G. Peyronel, G. C. Pellacani and A. Pignedoli, *Inorg. Chim. Acta* 1971, **5**, 627.