NICKEL(II) COMPLEXES WITH 1,3,6,9,11,14-HEXAAZATRICYCLO-(12,2,1,1)OCTADECANE. STRUCTURE AND SOME PROPERTIES

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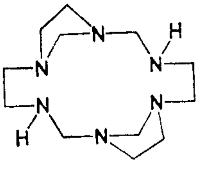
The following compounds have been prepared: $[NiL]Cl_2.3\,H_2O$, $[NiL]Br_2.3\,H_2O$, $[NiL]I_2.H_2O$ and $[NiL](NO_3)_2.H_2O$, where L is the title macroligand. The structure of $[NiL]I_2.H_2O$ was solved by direct methods with the results: $a = 8{\cdot}399(3)$, $b = 14{\cdot}501(2)$, $c = 15{\cdot}699(2)$ Å, $\alpha = 86{\cdot}64(1)°$, $\beta = 87{\cdot}46(3)°$, $\gamma = 89{\cdot}01(2)°$. The substance crystallizes in the triclinic system with space group $P\,1$, $Z = 4$, $R = 0{\cdot}0589$, $wR = 0{\cdot}0626$. The arrangement around the nickel atom is approximately square planar. Cyclic voltammetry demonstrated the possibility of oxidizing the nickel (II) complex and the diamagnetic sulphate $[NiL](SO_4)_2$ was prepared by the reaction of $[NiL]Cl_2.3\,H_2O$ with $Na_2S_2O_8$.

Considerable attention has been paid to the coordination compounds of nickel with polyazamacrocyclic ligands for quite some time. Recently[1] the preparation of a new macrocyclic ligand was described, with the following formula, which will be denoted in this publication by the symbol L: Simultaneously, the authors described



the preparation of two of its coordination compounds with the composition $[NiL]Cl_2$ . . $2\,H_2O$ and $[NiL](ClO_4)_2$. It is interesting that this ligand was coordinated through only four of the six nitrogen atoms in both these compounds. As some macrocyclic ligands can stabilize higher oxidation states of nickel[2], we prepared further nickel(II) complexes with this ligand and with suitable anions and attempted to oxidize these compounds.

EXPERIMENTAL

Diethylene triamine was the product of the Loba-Feinchemie Co. (Austria), sodium peroxodisulphate was supplied by the Reachim Co. (U.S.S.R.) and the remaining chemicals, of p.a. purity, were supplied by the Lachema Co. All chemicals were used without further modifications.

The infrared absorption spectra were recorded on the Specord M 80 instrument (Carl Zeiss, Jena) by the Nujol technique. The magnetic susceptibility was measured at laboratory temperature by the Guoy method on laboratory-designed magnetic scales, calibrated using $Hg[Co(NCS)_4]$. The electrical conductivity was measured on a Conductivity Meter OK 102/1 instrument (Radelkis, Budapest) at 20°C. Electrochemical measurements were carried out in a methanol solution containing 0·1M LiCl as background electrolyte. The concentration of the complex was 1·5 mmol l^{-1}. The cyclic voltammograms were measured on the Princeton Applied Research Model 273 EG and G potentiostat/galvanostat in a three-electrode arrangement. A glassy carbon (gC) working electrode with an area of 0·08 cm^2 and porosity of 1 to 3% was used. The refeernce electrode was a saturated calomel electrode and the auxiliary electrode was made of platinum foil with a large surface area. The potential scan rate was in the range 0·005 to 0·5 V/s. All potential values are related to the SCE.

X-Ray structural analysis was carried out using $[NiL]I_2.H_2O$, which was doubly recrystallized from water. Orange crystals, suitable for X-ray structural analysis, were obtained by slow evaporation of a saturated solution at a constant temperature of 15°C. The density was determined experimentally by the suspension method in a $CHBr_3$–C_2H_5OH mixture. The actual X-ray crystallographic study was carried out using a crystal with dimensions of 0·35 × 0·3: × 0·25 mm. Preliminary recording was carried out by the film method on a Weissenberg instrument with a precession chamber, and final recording on a four-ring CAD 4 diffractometer using MoK_α rediation at normal temperatures. No correction was made for absorption and extinction. Refinement method: block-diagonally in five blocks using the weighing scheme $2{\cdot}126/(\sigma^2(F) + 0{\cdot}0009\ F^2)$. The final values were $R = 0{\cdot}0589$, $wR = 0{\cdot}0626$. The H atoms were calculated to the expected positions. In the overall calculation of 385 refined parameters, all the nonhydrogen atoms were refined anisotropically except for C_2'' to C_5'', whose temperature parameters were refined isotropically. The temperature parameters of the H-atoms were assumed to equal 1·2 times the parameters of the atoms to which they were bonded. The maximum Δ/σ value for the final refinement was 0·015. The maximum residual electron density value on the differential map was found to be 2·49e/Å^3 (in the vicinity of the iodine atoms). The structure was solved using the SHELX 86, SHELX 76 and PARST programs on the EC 1033 computer.

$[NiL]Br_2.3\ H_2O$

An amount of 1·1 ml (10·5 mmol) of diethylene triamine in 10 ml methanol was added to a solution of 1·35 g (4·95 mmol) of $NiBr_2.3\ H_2O$ in 20 ml of methanol. The reaction mixture was stirred for 2 h at laboratory temperature; then 6 ml of 40% HCHO (0·08 mol) was added and the stirring was continued for a further 10 h. The mixture was left to stand overnight. The precipitated yellow crystals were drawn off, washed on the frit with methanol and ether and dried in a vacuum dessicator.

$[NiL]Cl_2.3\ H_2O$

This substance was prepared by slightly modifying the procedure described in the literature[1]. A solution of 2·4 g (10 mmol) of $NiCl_2.6\ H_2O$ in 25 ml methanol was mixed with a solution of 2·2 ml (21 mmol) of diethylene triamine in 5 ml of methanol. After stirring the mixture for one hour at laboratory temperature, 12 ml of a 40% aqueous solution of formaldehyde was added (0·16 mmol) and the reaction mixture was stirred for a further 6 h. After being left to stand for 24 h, the finely crystalline substance precipitated in the solution was drawn off, washed on the frit with methanol and ether and dried in a vacuum dessicator.

$[NiL]I_2.H_2O$

A solution of 1·7 ml (16·5 mmol) of diethylene triamine in 10 ml of methanol was added to a solution of 2·5 g (8 mmol) of NiI_2 in 20 ml of methanol at laboratory temperature; after stirring for two hours, 9·5 ml of a 40% aqueous solution of HCHO (0·126 mol) was added. The further treatment was similar as for the bromide.

$[NiL](NO_3)_2.H_2O$

This substance was prepared using a mixture of 2·9 g (10 mmol) of $Ni(NO_3)_2.6\,H_2O$ dissolved in 20 ml methanol, 2·1 ml (20 mmol) of diethylene triamine dissolved in 10 ml methanol and 12 ml of 40% formaldehyde (0·16 mol). The reaction mixture was treated by a procedure similar to the preparation of $[NiL]Br_2.3\,H_2O$. However, on standing, only a white powder was precipitated from this mixture; this powder was drawn off and the mother liquor was concentrated on a water bath and precipitated with ethanol. The precipitated, yellow powder was drawn off on a frit and washed with ethanol and ether.

$[NiL](SO_4)_2$

An amount of 0·4 g (0.9 mmol) of $[NiL]Cl_2.3\,H_2O$ was dissolved in 10 ml of water and the solution was cooled to almost 0°C. Then a total amount of 0·25 g (1·05 mmol) of $Na_2S_2O_8$ was added in small amounts with constant stirring. After 15 min a yellow substance was precipitated, drawn off and washed with ice water on the frit.

RESULTS AND DISCUSSION

The chemical compositions of the substances prepared are given in Table I. Halides with the compositions $[NiL]Cl_2 . 3\,H_2O$, $[NiL]Br_2 . 3\,H_2O$ and $[NiL]I_2 . H_2O$ are diamagnetic compounds, indicating that they have square planar arrangement. Thus, only four nitrogen atoms of the hexaazamacrocyclic ligand are coordinated and the halogens lie outside the coordination sphere. This conclusion was also confirmed by the results of X-ray structural analysis of the iodide $[NiL]I_2 . H_2O$. Table II lists the basic data for the structure solution. Important interatomic distances and angles are given in Table III; the coordinates of the nonhydrogen atoms and their temperature parameters are listed in Table IV. Figure 1 gives a perspective view of the complex molecule (the thermal ellipsoids are depicted with 50% probability). The system consists of a triclinic unit cell with relatively rare number of formula units $Z = 4$. This is possible because the structure contains three symmetrically independent molecules – two with nickel atoms lying at the centre of symmetry and the third in a general position.

The coordination polyhedron of the central atom is a square – the coordination bonds are equal in length within experimental error and the deviations of the atoms from an ideal plane through the Ni, N1, N2, N4 and N5 atoms are less than 0·03 Å. The N3 and N6 atoms and the iodine and oxygen atoms are not coordinated to the central atom. The macrocyclic ligand forms two five-membered and two six-membered cycles with the central atom.

The infrared spectra of these substances contain absorption maxima corresponding to the ν_{NH} and ν_{OH} (water) vibrations in the region from 3 030 to 3 480 cm^{-1} and to the δ_{OH} vibration at a wavenumber of 1 620 cm^{-1} (s) for chloride and bromide and 1 605 cm^{-1} (m) for iodide.

Nickel(II) complexes were prepared as the halides in an attempt to carry out the oxidation by the corresponding halogens. The reaction was carried out at laboratory temperature by introducing chlorine into a solution of $[NiL]Cl_2 . 3 H_2O$ in methanol or by adding a solution of iodine in methanol to a suspension of $[NiL]I_2 . H_2O$ in the same solvent. It follows from analysis of the reaction products and study of their magnetic and spectral properties, along with measurement of their molar conductivity that the halogen attacked the ligand under the given conditions and that the central Ni(II) atom was not oxidized. Consequently, the possibility of oxidizing this type of complex by cyclic voltammetry was studied. The experiment was carried out using the nitrate $[NiL](NO_3)_2 . H_2O$, where there is no danger of oxidation of the anion and which is readily soluble in the solvents used. This compound is also diamagnetic, characteristic for square planar complexes. The molar conductivity value of an aqueous solution with a concentration of $5 . 10^{-4}$ mol l^{-1} is 230 S cm^2 mol^{-1}, corresponding[5] to a 1 : 2 electrolyte. The infrared absorption

TABLE I

Chemical compositions of the substances prepared

Compound	Formula M_r	Calculated/Found				
		% Ni	% C	% H	% N	% Cl (Br)
$[NiL]Cl_2 . 3 H_2O$	$C_{12}H_{32}Cl_2N_6NiO_3$	13·40	32·90	7·36	19·19	16·19
	438·0	13·63	32·73	7·75	18·71	16·20
$[NiL]Br_2 . 3 H_2O$	$C_{12}H_{32}Br_2N_6NiO_3$	11·14	27·35	4·97	15·95	30·34
	529·9	11·56	26·65	5·09	15·34	30·02
$[NiL]I_2 . H_2O$	$C_{12}H_{28}I_2N_6NiO$	10·04	24·65	4·48	14·37	
	584·9	9·54	24·13	4·39	13·93	
$[NiL](NO_3)_2 . H_2O$	$C_{12}H_{28}N_8NiO_7$	12·90	31·*h*7	6·20	24·62	
	455·11	13·21	32·01	5·96	24·86	
$[NiL](SO_4)_2$	$C_{12}H_{26}N_6NiO_8S_2$	11·62	28·53	5·19	16·63	
	505·2	12·00	28·39	5·27	16·15	

spectrum of this compound contains the absorption maxima ν_3 – 1 375 cm^{-1} (vs) and ν_2 – 828 cm^{-1} (s) corresponding[6] to the ion-bonded NO_3 group. Results of study of this substance by cyclic voltammetry have shown that it can be oxidized in methanol solution (0·1 mol l^{-1} LiCl) (Fig. 2) at a gC electrode at a potential of 0·8 to 1 V. Two shoulders appeared on the cyclic voltammogram at low polarization rates (0·005 V/s) and coalesce into a single shoulder at potential growth rates of greater than 0·1 V/s. The heights of both peaks agree with the Faraday current values for both steps in the one-electron oxidation, obtained for analogous complex compounds[7] under the same conditions (ca 25 μA cm^{-2} for a one-electron exchange). The height of the anodic peak depends linearly on the square root of the rate of

TABLE II

Basic crystallographic data for $[NiL]I_2 . H_2O$

Crystallographic system, space group	triclinic, P I
Lattice parameters	a = 8·399(3) Å
	b = 14·501'(2)
	c = 15·699(2)
	α = 86·64(1)°
	β = 87·46(3)°
	γ = 88·01(2)°
Volume of unit cell	V = 1 906·8(8) Å^3
Number of formula units	Z = 4
Density (X-ray/exp)	2·037/2·05 g cm^{-3}
Linear absorption coefficient	μ = 4·29 mm^{-1}
F(000)	1 144
Crystal dimensions	0·35 nm 0·30 nm 0·25 mm
Radiation	MoK$_\alpha$ 0·7107 Å monochr. graphite
Diffractometer	CAD 4 (Enraf–Nonius)
Number of reflections	12 625 (6 330 unique)
Range of 2θ for refinement of the lattice parameters	38—40°
$2\theta_{max}$; h, j, k, l_{max}	50°; $h \leqq 9$, $k \leqq 17$, $l \leqq 18$
Scan type	$\omega/2\ \theta$
Control of crystal stability	after measuring 200 reflections
S value	2·41
Correction for anomalous disperions	not carried out
Computer programs	SHELX 76 (ref.[3]), SHELX 86 (ref.[3]), PARST (ref.[4])
Computer, temperature	EC 1033, 20°C
Final R-factor values	R = 0·0589, wR = 0·0626

electrode polarization. It can thus be concluded that a two-electron irreversible diffusion-controlled oxidation occurs. Better-defined cyclic voltammograms were obtained using dimethyl sulphoxide as solvent and confirmed the above results. The cyclic voltammogram of the base electrolyte indicated that no interference with the curve of the test complex is present.

Consequently, this type of nickel(II) complex can be oxidized using a sufficiently strong oxidizing agent. An attempt was made to electrochemically oxidize $[NiL](NO_3)_2 . H_2O$ dissolved in methanol under the conditions corresponding to its oxidation in cyclic voltammetry. However, the substance formed is not sufficiently stable in solution and was again reduced during attempts to isolate it.

Attempts at chemical oxidation were carried out using the chloride $[NiL]Cl_2 . 3\,H_2O$, to an aqueous solution of which was added solid $Na_2S_2O_8$ with cooling. A solid substance precipitated from the solution during mixing, and has the chemical formula $[NiL](SO_4)_2$ or $[NiL](S_2O_8)$. It is a diamagnetic compound, in agreement with valence sphere arrangement of t_{2g}^6 for Ni(IV), so that all the nickel(IV) substances so far prepared are diamagnetic. Under the preparation conditions employed, this substance is X-ray amorphous and could not be obtained in crystalline form for X-ray structural analysis. This substance is stable in the solid state and its thermal decomposition begins at a temperature of 140°C and is practically explosive. The infrared spectrum of this substance contains maxima at wavenumbers of 670 cm^{-1} (s), 968 cm^{-1} and 1 044 cm^{-1} (s), typical for the $(SO_4)^{2-}$ group[8] and the maxima found in the spectra of $Na_2S_2O_8$ are lacking. Iodine is precipitated from a potassium

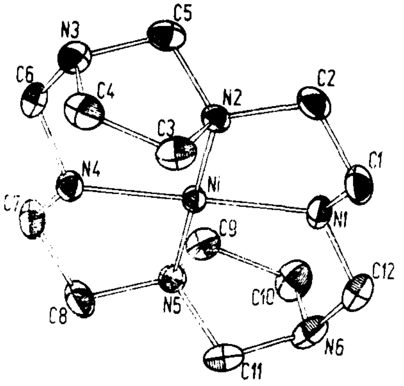


Fig. 1

Atom arrangement in the cation of the compound $[NiL]I_2 . H_2O$

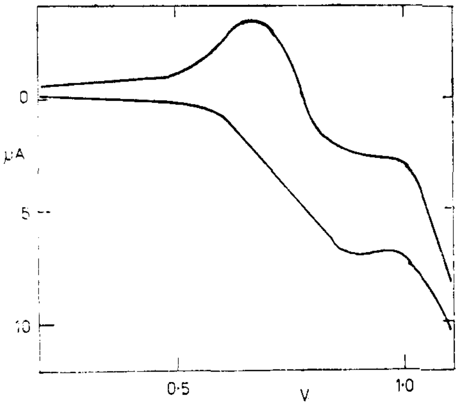


Fig. 2

Cyclic voltammogram of $[NiL](NO_3)_2 . H_2O$ (1·5 mmol l^{-1}). Electrolyte: 0·1 mol l^{-1} LiCl, scan rate 0·005 V/s

TABLE III

Important interatomic distance (Å) and angles (°)

Bond	Distance	Atoms	Angle
Ni1—N1	1·923(6)	N4—Ni1—N5	86·8(3)
Ni1—N2	1·951(7)	N2—Ni1—N5	178·1(3)
Ni1—N4	1·920(6)	N2—Ni1—N4	92·5(3)
Ni1—N5	1·934(8)	N1—Ni1—N5	93·8(3)
N1—C1	1·489(13)	N1—Ni1—N4	179·3(3)
N1—C12	1·500(12)	N1—Ni1—N2	86·9(3)
N2—C2	1·485(12)	Ni1—N1—C12	121·1(5)
N2—C3	1·480(12)	Ni1—N1—C1	106·9(6)
N2—C5	1·502(11)	C1—Ni1—C12	111·2(7)
N3—C4	1·489(13)	Ni1—N2—C5	112·3(5)
N3—C5	1·463(12)	Ni1—N2—C3	109·1(6)
N3—C6	1·409(13)	Ni1—N2—C2	108·9(6)
N4—C6	1·492(12)	C3—N2—C5	102·5(7)
N4—C7	1·489(12)	C2—N2—C5	110·6(7)
N5—C8	1·478(12)	C2—N2—C3	113·4(7)
N4—C9	1·512(11)	C5—N3—C6	112·9(7)
N5—C11	1·502(12)	C4—N3—C6	114·5(8)
N6—C10	1·465(14)	C4—N3—C5	101·6(7)
N6—C11	1·459(12)	Ni1—N4—C7	108·3(5)
N6—C12	1·440(13)	Ni1—N4—C6	118·4(5)
C1—C2	1·482(16)	C6—N4—C7	111·9(7)
C3—C4	1·520(14)	Ni1—N5—C11	112·8(6)
C7—C8	1·504(15)	Ni1—N5—C9	109·8(6)
C9—C10	1·578(3)	Ni1—N5—C8	109·1(5)
		C9—N5—C11	102·8(6)
		C8—N5—C11	109·7(7)
		C8—N5—C9	112·6(7)
		C11—N6—C12	114·1(7)
		C10—N6—C12	115·3(8)
		C10—N6—C11	103·2(8)
		N1—C1—C2	107·2(8)
		N2—C2—C1	107·4(8)
		N2—C3—C4	105·4(8)
		N3—C4—C3	106·4(8)
		N2—C5—N3	103·7(7)
		N3—C6—N4	115·4(7)
		N4—C7—C8	106·0(8)
		N5—C8—C7	106·7(8)
		N5—C9—C10	102·7(7)
		N6—C10—C9	106·4(8)
		N5—C11—N6	103·6(7)
		N1—C12—N6	114·3(8)

TABLE III
(*Continued*)

Bond	Distance	Atoms	Angle
Ni′—N′1	1·930(6)	N′1—Ni′—N′2	86·9(3)
Ni′—N′2	1·938(7)	Ni′—N′1—C′1	107·7(5)
N′1—C′1	1·469(12)	Ni′—N′2—C′5	112·5(6)
N′2—C′2	1·491(11)	Ni′—N′2—C′3	109·6(5)
N′2—C′3	1·518(12)	Ni′—N′2—C′2	108·4(5)
N′2—C′5	1·489(11)	C′3—N′2—C′5	101·9(6)
N′3—C′4	1·460(13)	C′2—N′2—C′5	109·8(7)
N′3—C′5	1·455(12)	C′2—N′2—C′3	114·6(7)
N′3—C′6	1·451(12)	C′5—N′3—C′6	112·5(7)
C′1—C′2	1·502(14)	C′4—N′3—C′6	115·5(7)
C′3—C′4	1·540(13)	C′4—N′3—C′5	103·2(7)
		N′2—C′3—C′4	104·1(7)
		N′3—C′4—C′3	106·6(8)
		N′2—Cl5—N′3	104·5(7)
		N′2—C′2—C′1	106·8(8)
		N′1—C′1—Cl2	106·3(7)
Ni″—N″1	1·929(8)	N″1—Ni″—N″2	85·8(3)
Ni″—N″2	1·935(7)	Ni″—N″1—C″1	108·8(6)
N″1—C″1	1·500(12)	Ni″—N″2—C″5	110·7(5)
N″2—C″2	1·501(16)	Ni″—N″2—C″3	111·3(7)
N″2—C″3	1·500(11)	Ni″—N″2—C″2	110·9(6)
N″2—C″5	1·501(11)	C″3—N″2—C″5	104·9(7)
N″3—C″4	1·470(14)	C″2—N″2—C″5	108·1(6)
N″3—C″5	1·449(13)	C″2—N″2—C″3	110·7(8)
N″3—C″6	1·421(15)	C″5—N″3—C″6	112·8(7)
C″1—C″2	1·500(14)	C″4—N″3—C″6	110·4(9)
C″3—C″4	1·540(15)	C″4—N″3—C″5	102·8(8)
		N″1—C″1—C″2	106·1(8)
		N″2—C″2—C″1	106·2(8)
		N″2—C″2—C″1	106·2(8)
		N″2—C″3—C″4	100·8(8)
		N″3—C″4—C″3	109·6(8)
		N″2—C″5—N″3	103·4(7)

iodide solution acidified with hydrochloric acid. When washed with water at laboratory temperature, addition of barium chloride permits precipitation of $BaSO_4$. No further barium sulphate is precipitated after separation of this substance and acidification and boiling of the filtrate. Thus, this substance was assigned the chemical formula $[NiL](SO_4)_2$.

TABLE IV

Fractional coordinates of the nonhydrogen atoms (. 10^4) and their anisotropic temperature parameters U_{ij} (. 10^2)

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni1	7568(1)	−0207(1)	2465(1)	2·81(5)	2·91(5)	2·23(5)	−0·28(4)	0·20(4)	−0·31(4)
N1	8956(8)	−0204(5)	1457(4)	3·4(4)	4·7(4)	3·1(4)	−0·01(3)	0·7(3)	0·7(3)
N2	9017(8)	0674(5)	2899(4)	3·0(4)	3·0(4)	3·5(4)	0·1(3)	−0·1(3)	−0·6(3)
N3	7377(10)	1173(5)	4023(5)	6·1(5)	3·9(4)	3·9(4)	−0·4(3)	0·3(3)	0·3(4)
N4	6195(8)	−0197(5)	3475(4)	3·7(4)	4·3(4)	2·6(4)	−0·5(3)	0·3(3)	−0·6(3)
N5	6153(9)	−1110(5)	2064(4)	4·5(4)	3·3(4)	2·6(4)	−0·4(3)	−0·1(3)	−0·3(3)
N6	7697(10)	−1551(6)	0885(5)	5·9(5)	5·0(5)	4·5(5)	−1·7(4)	−0·6(4)	2·0(4)
C1	0532(12)	0128(8)	1700(7)	4·5(6)	6·1(7)	5·1(6)	0·4(5)	2·0(5)	0·2(5)
C2	0224(11)	0943(7)	2214(7)	3·5(5)	4·0(5)	6·6(7)	0·4(5)	0·4(5)	−1·0(4)
C3	9718(12)	0261(7)	3681(6)	4·9(6)	4·4(5)	4·5(6)	−0·5(4)	−1·5(5)	0·6(4)
C4	8672(12)	0603(7)	4416(6)	5·8(6)	5·1(6)	3·9(6)	0·0(4)	−1·7(5)	−0·2(5)
C5	8157(11)	1512(6)	3216(6)	4·4(6)	3·6(5)	5·1(6)	0·0(4)	−0·5(5)	0·1(4)
C6	5970(11)	0688(7)	3908(6)	4·7(6)	5·2(6)	3·5(5)	−0·9(4)	1·4(4)	−0·1(5)
C7	4646(11)	−0606(8)	3284(6)	4·0(6)	6·7(7)	3·9(5)	−1·1(5)	1·3(4)	−1·7(5)
C8	5053(13)	−1432(7)	2776(6)	6·0(7)	5·4(6)	3·6(5)	−0·4(5)	0·7(5)	−2·5(5)
C9	5288(11)	−0699(8)	1304(5)	4·5(5)	4·8(6)	3·2(4)	−0·5(4)	−0·9(4)	0·6(4)
C10	6361(14)	−1022(8)	0523(6)	7·2(8)	8·0(8)	3·1(5)	−1·2(5)	−0·8(5)	1·2(6)
C11	7030(12)	−1922(6)	1706(6)	5·4(6)	3·2(5)	5·6(6)	−0·7(4)	−0·9(5)	0·6(4)
C12	9141(11)	−1042(7)	0943(6)	4·5(6)	6·0(6)	4·2(5)	−1·6(5)	0·2(4)	1·1(5)

TABLE IV
(*Continued*)

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I1	4513(1)	1964(0)	1788(0)	4·29(4)	4·78(4)	4·43(4)	−0·16(3)	0·03(3)	0·73(3)
I2	2663(1)	6932(0)	1229(0)	6·17(4)	4·26(4)	4·60(4)	−0·36(3)	−0·76(3)	−0·65(3)
I3	−2409(1)	7973(1)	4970(1)	5·94(5)	5·16(4)	6·83(5)	0·10(4)	0·00(4)	−1·35(3)
I4	8124(1)	5801(0)	2905(0)	7·56(5)	4·47(4)	4·85(4)	−0·45(3)	0·98(4)	0·13(2)
O1	7626(9)	1306(5)	0396(5)	6·4(5)	6·3(5)	6·5(5)	1·5(4)	1·1(4)	1·7(4)
O2	9552(12)	1961(6)	6983(6)	10·3(8)	6·7(6)	8·4(6)	−1·3(5)	−1·2(5)	−0·9(5)
Ni′	0000(0)	5000(0)	0000(0)	2·9(1)	2·7(1)	3·0(1)	−0·4(1)	−0·2(1)	−0·5(1)
N′1	1621(8)	5254(5)	−0889(4)	2·8(4)	3·4(4)	3·9(4)	0·0(3)	0·0(3)	−0·1(3)
N′2	1395(8)	4019(5)	0431(4)	3·2(4)	2·9(4)	4·04(4)	−0·7(3)	−0·3(3)	0·8(3)
N′3	−0391(9)	3250(5)	1389(5)	4·6(5)	3·4(4)	4·1(4)	−0·1(3)	0·2(4)	0·3(3)
C′1	3127(11)	4846(7)	−0595)6(	3·8(5)	4·4(5)	5·0(6)	0·2(4)	0·3(4)	1·0(4)
C′2	2737(11)	3900(7)	−0209(6)	3·7(5)	5·0(6)	4·7(6)	−0·4(5)	0·5(4)	1·4(4)
C′3	1903(12)	4226(6)	1315(6)	5·5(6)	3·0(5)	4·8(6)	−0·7(4)	−1·2(5)	0·3(4)
C′4	0717(12)	3689(7)	1925(6)	5·5(6)	4·3(5)	3·1(5)	−0·6(4)	−0·9(4)	0·3(4)
C′5	0553(11)	3128(6)	0603(6)	4·4(5)	2·8(5)	4·5(5)	−1·1(4)	−1·4(4)	0·3(4)
C′6	−1868(11)	3756(6)	1243(6)	3·9(5)	3·9(5)	5·1(6)	0·2(4)	−0·2(4)	−0·5(4)
Ni″	5000(0)	5000(0)	5000(0)	3·2(1)	2·7(1)	3·0(1)	−0·2(1)	−0·4(1)	0·1(1)
N″1	4849(9)	3965(5)	4291(5)	4·4(5)	4·0(4)	4·6(5)	−1·2(4)	−0·6(4)	0·7(4)
N″2	3211(9)	5521(4)	4392(4)	4·8(5)	4·0(4)	4·0(4)	−0·4(3)	−0·6(3)	0·8(4)
N″3	2465(12)	6666(5)	5303(6)	10·2(9)	6·3(7)	9·5(9)	0·1(6)	−0·9(7)	0·6(6)
C″1	3949(13)	4267(6)	3516(5)	15(1)	11(1)	3·6(6)	−3·0(7)	1·6(7)	−7·9(9)
C″2	2552(9)	4830(9)	3831(10)	11·4(6)					
C″3	3661(18)	6391(6)	3880(7)	9·0(4)					
C″4	3188(17)	7122(8)	4522(6)	8·3(4)					
C″5	1900(9)	5808(7)	5006(6)	8·0(4)					
C″6	3616(12)	6527(7)	5936(7)	5·8(7)	5·3(7)	10·(1)	−0·7(7)	1·2(7)	2·2(6)

It follows from these results that this type of nickel(II) complex can be oxidized. Cyclic voltammetry indicates that stronger oxididizing agents are required for this purpose and that agents that do not attack the ligand must be used.

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