Co-ordination Chemistry of Higher Oxidation States. Part 7.[1] Nickel(III) and Nickel(II)–Nickel(IV) Complexes of Ethylenediamine and Related Ligands. A Clarification †

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The chlorination of $Ni(en)_2Cl_2$ (en = ethylenediamine) in alcohol is shown to yield either the nickel(III) complex *trans*-$[Ni(en)_2Cl_2]Cl$ or the mixed-valence class II compound $[\mathrm{Ni^{II}(en)_2Ni^{IV}(en)_2Cl_2}]Cl_4$ depending upon the conditions, and the confusion in the literature over the nature of these materials is corrected. Data are reported for the related complexes $[\mathrm{Ni^{III}(en)_2Br_2}]Br$, $[\mathrm{Ni^{III}(pd)_2X_2}]X$, $[\mathrm{Ni^{II}(pn)_2Ni^{IV}(pn)_2Cl_2}]Cl_4$ [pd = $H_2N(CH_2)_3NH_2$, pn = $H_2NCH_2CH(CH_3)NH_2$; X = Cl or Br], $[\mathrm{Ni^{III}(en)_2Cl_2}]ClO_4$, and $[\mathrm{Ni^{II}(en)_2Ni^{IV}(en)_2Cl_2}][ClO_4]_4$. Attempts to isolate $\mathrm{Ni^{III}}$ or $\mathrm{Ni^{II}}$–$\mathrm{Ni^{IV}}$ complexes with $Me_2N(CH_2)_2NMe_2$ or *o*-$C_6H_4(NMe_2)_2$ failed.

Babaeva *et al.*[2] reported that treatment of nickel(II) ethylenediamine (en) complexes $Ni(en)_2X_2$ with halogens in methanol gave nickel(III) complexes $Ni(en)_2X_3$ (X = Cl or Br). In subsequent papers more details on these complexes, and analogues with other diprimary amines were reported.[3-6] It was shown that the complexes were of two types: type A which had magnetic moments *ca.* 2 B.M. and exhibited strong e.s.r. spectra, and type B with $\mu_{eff.} \leqslant 0.9$ B.M. and giving only weak e.s.r. signals. The difference between the two types was not satisfactorily explained. Recently Yamashita *et al.*[7] suggested that type A complexes [including $Ni(en)_2Cl_3$] are 'genuine' $\mathrm{Ni^{III}}$, and type B are $\mathrm{Ni^{II}}$–$\mathrm{Ni^{IV}}$ mixed-valence class II compounds. This was disputed by Papavassiliou and Layek [8] who assigned a $\mathrm{Ni^{II}}$–$\mathrm{Ni^{IV}}$ structure to '$Ni(en)_2Cl_3$', and suggested that Yamashita's $\mathrm{Ni^{III}}$ complex was a ligand-deficient material. As an extension of our studies [9] on palladium(IV) complexes we have examined $\mathrm{Ni^{III}}$ and $\mathrm{Ni^{IV}}$ complexes of phosphine and arsine ligands, and prepared the ethylenediamine compounds for comparison, finding that two 'forms' of $Ni(en)_2Cl_3$ can indeed be obtained. We report these results here along with data on some related systems.

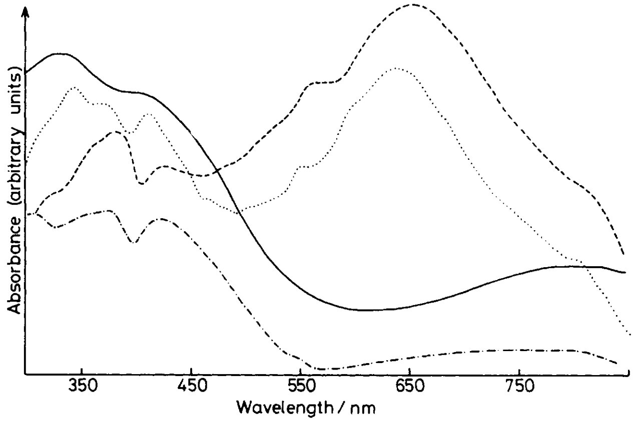

Figure 1. Diffuse-reflectance spectra of $[\mathrm{Ni^{III}(en)_2Cl_2}]Cl$ (— · —); $[\mathrm{Ni^{II}(en)_2Ni^{IV}(en)_2Cl_2}]Cl_4$ (· · · ·); $[Ni(pd)_2Cl_2]Cl$ (——), and $[Ni(pn)_2Cl_2]Cl$ (- - - -) in the range 300—850 nm. Barium sulphate was used as diluent and reference

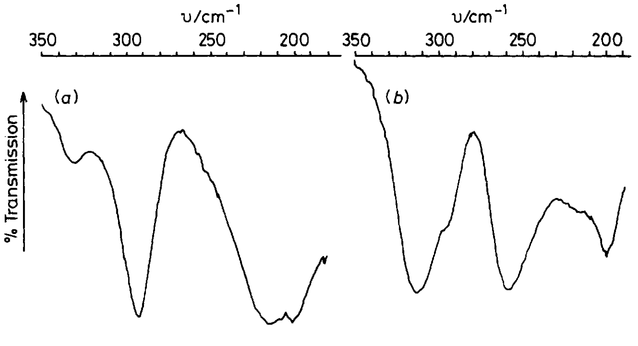

Figure 2. Far-i.r. spectra (350—180 cm^{-1}) of (*a*) $[\mathrm{Ni^{III}(en)_2Cl_2}]Cl$ and (*b*) $[\mathrm{Ni^{II}(en)_2Ni^{IV}(en)_2Cl_2}]Cl_4$ in Nujol mulls

Results and Discussion

Rapid chlorination of a saturated solution of $Ni(en)_2Cl_2$ in wet methanol (technical grade MeOH containing *ca.* 1% H_2O) produced a brownish yellow powder, whilst bubbling a slow stream of chlorine heavily diluted with nitrogen through a solution of $Ni(en)_2Cl_2$ in MeOH–EtOH (1 : 1 v/v) gave a green-black solid.‡ Both compounds are insoluble in, or decomposed by organic solvents limiting measurements to the solid state. Analytically both materials correspond to a $Ni(en)_2Cl_3$ formulation, but have very different spectroscopic and magnetic properties. The brown-yellow form has $\mu_{eff.} = 1.9$ B.M., and gives a strong e.s.r. signal at room temperature characteristic of a tetragonally distorted d^7 ($t_{2g}^6e_g^1$) ion ($g_{\parallel}$ *ca.* 2, $g_{\perp}$ *ca.* 2.2). The green-black form has $\mu_{eff.}$ *ca.* 0.9 B.M.§ and exhibits an e.s.r. signal only under high sensitivity (*cf.* ref. 5). The diffuse-reflectance spectrum of the yellow-brown complex (Figure 1, Table) is similar to those of other pseudo-octahedral $\mathrm{Ni^{III}}$ complexes such as $[Ni(L)X_2]ClO_4$ (L = 2,3-dimethyl-1,4,8,11-tetra-azacyclotetradecane) [12] and $[Ni(Me_2PCH_2CH_2PMe_2)_2Cl_2]BF_4$,[13] and its far-i.r. spectrum (Figure 2) contains a band at 214 cm^{-1} assignable as ν(NiCl); the low vibration

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† *Non-S.I. units employed:* 1 B.M. = 0.927×10^{-23} A m^2; 1 G = 10^{-4} T.

‡ The colour of the mixed-valence complexes depends upon the state of subdivision, ranging from a copper colour in crystals, green-black as a powder, and blue on grinding on paper (*cf.* refs. 10 and 11).

§ The origin of these small magnetic moments is unclear (see refs. 3 and 7).

Table. Spectroscopic data

Complex	I.r.[a](ν/cm^{-1})	$E_{max.}$ [b]/nm	E.s.r.[c]
$[Ni(en)_2Cl_2]Cl$	214s	778vbr, 530w (sh), 438 (sh), 420, 374, 354 (sh), 306	$g_{\parallel}$ = 2.03 $g_{\perp}$ = 2.185 (63)
$[Ni(en)_2Cl_2]ClO_4$	215s	800br, 530vw (sh), 382 (sh), 366 (sh), 336, 274 (sh)	g = 2.137 (275)
$[Ni(pd)_2Cl_2]Cl$	216s	826, 530w (sh), 420br, 380, 354 (sh), 322 (sh), 302 (sh)	$g_{\parallel}$ = 2.039 $g_{\perp}$ = 2.174 (43)
$[Ni(en)_2Br_2]Br$		850, 560 (sh), 405 (sh), 380, 250	g = 2.12 (355)
$[Ni(pd)_2Br_2]Br$		950 (sh), 850br, 576 (sh), 510br, 442br (sh), 394 (sh), 378 (sh), 352 (sh)	g = 2.129 (360)
$[Ni(en)_2Ni(en)_2Cl_2]Cl_4$	254s	800 (sh), 720 (sh), 670 (sh), 640, 612 (sh), 558, 412, 370, 344, 328 (sh)	g = 2.16 (283)
$[Ni(en)_2Ni(en)_2Cl_2][ClO_4]_4$	*ca.* 250 (sh)	838w, 580s, 450 (sh), 358, *ca.* 280 (sh)	g_1 = 2.414 g_2 = 2.184 (65) g_3 = 2.019
$[Ni(pn)_2Ni(pn)_2Cl_2]Cl_4$	250s	794w (sh), 720 (sh), 648s, 622 (sh), 558 (sh), 422, 378, 322	No detectable signal
$[Ni(pn)_2Ni(pn)_2Br_2]Br_4$	204s	1 000, 970 (sh), 770 (sh), 690br (sh), 616 (sh), 446, 382	No detectable signal
$[Ni\{o\text{-}C_6H_4(PMe_2)(NMe_2)\}_2Br_2]ClO_4$			$g_{\parallel}$ = 2.05 $g_{\perp}$ = 2.176 (54)
$[Ni\{o\text{-}C_6H_4(PMe_2)(NMe_2)\}_2Cl_2]ClO_4$			$g_{\parallel}$ = 2.05 $g_{\perp}$ = 2.264 (90)

[a] Polythene plates, 400—180 cm^{-1}, Nujol mulls. Bands assigned to ν(Ni–X) (Ni^{III} complexes) or $\nu(Ni^{IV}–X \cdots Ni^{II})$ (mixed-valence $Ni^{II}–Ni^{IV}$ complexes). [b] Diffuse reflectance, with dried $BaSO_4$ as diluent and reference. [c] Recorded at room temperature. Spectra recorded on powders in quartz tubes except for the Ni^{III}–o-$C_6H_4(PMe_2)(NMe_2)$ complexes which were generated *in situ* by addition of X_2–CCl_4 to a CH_2Cl_2 solution of the appropriate Ni^{II} complex. Linewidths/G (derivative peak to peak) are shown in parentheses.

frequency is similar to those of D_{4h} $[Ni(L–L)_2Cl_2]^+$ (L–L = bidentate phosphine or arsine [13,14]). The green-black form has an electronic spectrum dominated by a broad band centred at *ca.* 640 nm assignable to intervalence charge transfer $Ni^{II} \longrightarrow Ni^{IV}$,[7,8] and the strong i.r. band at 254 cm^{-1} is the $Ni^{II} \cdots Cl \cdots Ni^{IV}$ stretching vibration. Thus the brown-yellow form is a genuine Ni^{III} complex, $[Ni(en)_2Cl_2]Cl$, and the green-black isomer a mixed-valence class II complex $[Ni^{II}(en)_2Ni^{IV}(en)_2Cl_2]Cl_4$. The confusion in the literature over these two forms arises both from their quite similar methods of preparation (mixtures are readily obtained by small changes in the reaction conditions) and from the fact that the preparations used by previous workers [2,3,7,8] have not been described in detail. The 'Ni^{III}' complex is sometimes obtained with a greenish hue due to the presence of some of the Ni^{II}–Ni^{IV} form (evident in the electronic spectrum), and all the samples of $[Ni^{II}(en)_2Ni^{IV}(en)_2Cl_2]Cl_4$ we have obtained give weak e.s.r. signals due to traces of Ni^{III}.

Bromination of $Ni(en)_2Br_2$ with Br_2 in CCl_4, in MeOH, or 1 : 1 MeOH–EtOH mixtures under a variety of conditions gave a red-brown solid which was identified as the nickel(III) complex $[Ni(en)_2Br_2]Br$. We have not been able to obtain a Ni^{II}–Ni^{IV} form, although in view of the results with the chloride system, the existence of the latter cannot be certainly ruled out.

The halogenation of $Ni(pd)_2X_2$ [pd = $H_2N(CH_2)_3NH_2$; X = Cl or Br] gave only Ni^{III} complexes $[Ni(pd)_2X_2]X$, whilst $Ni(pn)_2X_2$ [pn = $H_2NCH_2CH(CH_3)NH_2$] formed mixed-valence $[Ni^{II}(pn)_2Ni^{IV}(pn)_2X_2]X_4$ (Table), these results being generally consistent with the literature,[2,7,8] although the spectra (Table) have not been reported fully previously. Attempts to obtain a second form of any of the pd or pn complexes have been unsuccessful. The reaction of $[Ni^{III}(en)_2Cl_2]Cl$ with 30% $HClO_4$ gives $[Ni^{III}(en)_2Cl_2]ClO_4$,[2] but on repeated treatment with 70% $HClO_4$ the product is $[Ni^{II}(en)_2Ni^{IV}(en)_2Cl_2][ClO_4]_4$.[7] Our data (Table) confirm these formulations, and the preparation of these materials indicates again the subtle balance between Ni^{III} and Ni^{II}–Ni^{IV} in these systems. The formation of $[Ni^{II}(en)_2Ni^{IV}(en)_2Cl_2]Cl_4$ requires the generation of $Ni^{IV}(en)_2Cl_4$, at least transiently in solution,* but attempts to isolate the pure Ni^{IV} complex by chlorination at low temperatures (*ca.* −80 °C), or using other oxidants (*e.g.* $K_2S_2O_8$), have been unsuccessful. It is probable that the pure $Ni(en)_2Cl_4$ is not stable, and that the Ni^{IV} entity is greatly stabilised in the mixed-valence compounds. Similar observations have been made in the Pd^{II}–Pd^{IV} systems.[10,15]

The nickel(II) complexes of *NN'*-alkylated diamines $[Ni(Me_2NCH_2CH_2NMe_2)Cl_2]$,[16] $[Ni\{o\text{-}C_6H_4(NMe_2)_2\}(H_2O)_2Cl_2]$,[17] and of 2,2'-bipyridyl and 1,10-phenanthroline (L-L), $[Ni(L–L)_2Cl_2]$,[18,19] were not oxidised by chlorine or nitric acid and $[Ni\{o\text{-}C_6H_4(AsMe_2)(NMe_2)\}_2Cl_2]$[17] immediately decomposed with oxidation of the ligand. *In situ* oxidation of dichloromethane solutions of $[Ni\{o\text{-}C_6H_4(PMe_2)(NMe_2)\}_2Cl]ClO_4$ and $[Ni\{o\text{-}C_6H_4(PMe_2)(NMe_2)\}_2][BF_4]_2$ with Cl_2 or Br_2 gave solutions with e.s.r. spectra characteristic of tetragonal Ni^{III} complexes, but these solutions decomposed rapidly and no solids have been isolated.

Experimental

Physical measurements were made as described previously.[20] Electronic spectra were recorded using a Perkin-Elmer model 554 spectrophotometer. E.s.r. spectra were recorded using a Varian E-4 *X*-band spectrometer with pitch–KCl as reference standard and 100-kHz modulation. I.r. spectra were obtained using KBr plates (4 000—400 cm^{-1}) and Polythene plates (400—180 cm^{-1}) in view of the oxidising nature of the complexes towards CsI. Nickel(II) starting materials were prepared by the literature method [21] or minor modifications thereof. Where indicated, MeOH and EtOH were dried by reflux

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* The corresponding Pd^{II}–Pd^{IV} and Pt^{II}–Pt^{IV} analogues exist in solution as mixtures of the constituents, the characteristic mixed-valence behaviour being limited to the solid state.[10,11]

over and distillation from their respective alkoxides. Other solvents were dried by conventional methods.

Nickel(III) *Complexes*.—(*i*) [Ni(en)$_2$Cl$_2$]Cl. A saturated solution of Ni(en)$_2$Cl$_2$ in MeOH was obtained by boiling excess Ni(en)$_2$Cl$_2$ with the solvent, cooling to room temperature and filtering. Chlorine gas was passed quickly through the solution with rapid magnetic stirring, resulting in immediate deposition of a brownish yellow precipitate. This was filtered off, washed well with MeOH, then diethyl ether, and dried *in vacuo* (Found: C, 17.0; H, 5.2; N, 19.3. $C_4H_{16}Cl_3N_4Ni$ requires C, 16.8; H, 5.6; N, 19.6%). Cautious treatment with 30% HCl followed by washing with MeOH resulted in a smaller yield of purer material (Found: C, 16.9; H, 5.4; N, 19.5%). $\mu_{\text{eff.}} = 1.87$ B.M.

(*ii*) [Ni(en)$_2$Cl$_2$]ClO$_4$. Prepared by the method of Babaeva *et al.*[2] (Found: C, 13.5; H, 4.8; N, 15.2. $C_4H_{16}Cl_3N_4NiO_4$ requires C, 13.8; H, 4.6; N, 16.0%). $\mu_{\text{eff.}} = 1.97$ B.M.

(*iii*) [Ni(pd)$_2$Cl$_2$]Cl. Prepared in an analogous fashion to [Ni(en)$_2$Cl$_2$]Cl (Found: C, 23.2; H, 6.2; N, 17.6. $C_6H_{20}Cl_3N_4Ni$ requires C, 23.0; H, 6.4; N, 17.9%). $\mu_{\text{eff.}} = 1.98$ B.M.

(*iv*) [Ni(en)$_2$Br$_2$]Br. To a suspension of finely ground Ni(en)$_2$Br$_2$ (0.5 g, 1.5 mmol) in a small volume of dry CCl$_4$ was added a slight excess of Br$_2$ (3% v/v) in the same solvent. After standing for 2 h the resultant brown solid was filtered off, washed repeatedly with small volumes of CCl$_4$, then dried *in vacuo*. Yield *ca.* quantitative (Found: C, 11.6; H, 3.7; N, 13.6. $C_4H_{16}Br_3N_4Ni$ requires C, 11.5; H, 3.9; N, 13.4%). $\mu_{\text{eff.}} = 1.80$ B.M.

(*v*) [Ni(pd)$_2$Br$_2$]Br. Prepared analogously from Ni(pd)$_2$Br$_2$ (Found: C, 16.2; H, 4.5; N, 12.3. $C_6H_{20}Br_3N_4Ni$ requires C, 16.1; H, 4.5; N, 12.5%). $\mu_{\text{eff.}} = 2.06$ B.M.

Nickel(II)-*Nickel*(IV) *Mixed-valence Complexes*.—(*i*) [Ni(en)$_2$Ni(en)$_2$Cl$_2$]Cl$_4$. A saturated solution of Ni(en)$_2$Cl$_2$ was prepared in a 1 : 1 mixture of dry MeOH and dry EtOH. Dry N$_2$ was passed over a dilute solution of Cl$_2$ in CCl$_4$ and the resultant dilute Cl$_2$–N$_2$ mixture slowly bubbled through the Ni(en)$_2$Cl$_2$ solution. The colour changed from dark blue through light green to dark green over *ca.* 30 min. After a further 5 min, dark green material slowly precipitated. This was filtered off, washed with dry EtOH, then diethyl ether, and dried *in vacuo* (Found: C, 17.0; H, 4.5; N, 19.4. $C_8H_{32}Cl_6N_8Ni_2$ requires C, 16.8; H, 5.6; N, 19.6%). $\mu_{\text{eff.}} = 0.92$ B.M.

(*ii*) [Ni(pn)$_2$Ni(pn)$_2$Cl$_2$]Cl$_4$. Prepared as very dark blue-green microcrystals as described by Babaeva *et al.*[3] (Found: C, 23.2; H, 6.4; N, 18.0. $C_{12}H_{40}Cl_6N_8Ni_2$ requires C, 23.0; H, 6.4; N, 17.9%). $\mu_{\text{eff.}} = 0.98$ B.M.

(*iii*) [Ni(en)$_2$Ni(en)$_2$Cl$_2$][ClO$_4$]$_4$. Prepared as a dark olive-green powder as described by Yamashita *et al.*[7] (Found: C, 11.8; H, 3.9; N, 13.4. $C_8H_{32}Cl_6N_6Ni_2O_{16}$ requires C, 11.6; H, 3.9; N, 12.7%). $\mu_{\text{eff.}} = 1.2$ B.M.

(*iv*) [Ni(pn)$_2$Ni(pn)$_2$Br$_2$]Br$_4$. Prepared as described by Papavassiliou and Layek,[8] except that a saturated solution of Ni(pn)$_2$Br$_2$ in dry MeOH–EtOH (1 : 1) was used. The complex was obtained as khaki-green reflective microcrystals (Found: C, 15.9; H, 4.6; N, 12.4. $C_{12}H_{40}Br_6N_8Ni_2$ requires C, 16.1; H, 4.5; N, 12.4%).

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References

1 Part 6, L. R. Gray, D. J. Gulliver, W. Levason, and M. Webster, *Acta Crystallogr.*, in the press.
2 A. V. Babaeva, I. B. Baranovskii, and G. G. Afanas'eva, *Russ. J. Inorg. Chem.*, 1965, **10**, 686.
3 A. V. Babaeva, V. I. Belova, Ya. K. Syrkin, and G. G. Afanas'eva, *Russ. J. Inorg. Chem.*, 1968, **13**, 660.
4 I. B. Baranovskii and G. Ya. Mazo, *Russ. J. Inorg. Chem.*, 1975, **20**, 244.
5 G. M. Larin, A. V. Babaeva, M. E. Dyatkina, and Ya. K. Syrkin, *Zh. Strukt. Khim.*, 1969, **10**, 427.
6 G. M. Larin and D. E. Dyatkina, *Dokl. Akad. Nauk. SSSR*, 1970, **191**, 841.
7 M. Yamashita, N. S. Kida, Y. Hamaue, and R. Aoki, *Inorg. Chim. Acta*, 1981, **52**, 43.
8 G. C. Papavassiliou and D. Layek, *Z. Naturforsch., Teil B*, 1982, **37**, 1406.
9 L. R. Gray, D. J. Gulliver, W. Levason, and M. Webster, *J. Chem. Soc., Dalton Trans.*, 1983, 133 and refs. therein.
10 R. J. H. Clark and W. R. Trumble, *Inorg. Chem.*, 1976, **15**, 1030.
11 R. J. H. Clark and M. Kurmoo, *Inorg. Chem.*, 1980, **19**, 3522; J. R. Campbell, R. J. H. Clark, and P. C. Turtle, *Inorg. Chem.*, 1978, **17**, 3622.
12 E. S. Gore and D. H. Busch, *Inorg. Chem.*, 1973, **12**, 1.
13 S. J. Higgins and W. Levason, unpublished work.
14 K. Konya and K. Nakamoto, *Spectrochim. Acta, Part A*, 1973, **29**, 1965.
15 N. Matsumoto, M. Yamashita, and S. Kida, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2334.
16 L. Sacconi, I. Bertini, and F. Mani, *Inorg. Chem.*, 1967, **6**, 262.
17 W. Levason and K. G. Smith, *Inorg. Chim. Acta*, 1980, **41**, 133.
18 P. Pfeiffer, V. Dominik, A. Fritzen, and B. Werdelmann, *Z. Anorg. Allg. Chem.*, 1949, **260**, 84.
19 R. H. Lee, E. Griswold, and J. Kleinberg, *Inorg. Chem.*, 1964, **3**, 1278 and refs. therein.
20 D. J. Gulliver, W. Levason, K. G. Smith, M. Selwood, and S. G. Murray, *J. Chem. Soc., Dalton Trans.*, 1980, 1872.
21 H. M. State, *Inorg. Synth.*, 1960, **6**, 198.

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