Reactions of Nickel(II) Complexes containing Arsine Ligands with Electron-deficient Olefins. Dianionic and Neutral Olefin Ligands in Nickel(II) and Nickel(III) Complexes

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The reaction of $[Ni_2(bdpa)_3(H_2O)][ClO_4]_4$ [bdpa = bis(3-dimethylarsinopropyl)phenylarsine] with tetracyanoethylene (tcne) in dichloromethane yields the diamagnetic planar $[Ni_2(bdpa)_2(tcne)][ClO_4]_2$ complex, from which can be obtained the BPh_4^- and PF_6^- derivatives. Infrared spectra and other measurements allow the assignment of a *cis*-bridging dianionic $tcne^{2-}$ ligand. Reaction of $[Ni_2(bdpa)_3(H_2O)][ClO_4]_4$ with 7,7,8,8-tetracyanoquinodimethane (tcnq) in a 1 : 3 ratio gives the planar $[Ni(bdpa)(tcnq)]ClO_4$; this, and the BPh_4^- derivative, are diamagnetic and contain the *cis*-bridging $tcnq^{2-}$ dianion. Employing greater amounts of tcnq in this reaction yields the d^7 nickel(III) five-co-ordinate species $[Ni_2(bdpa)_2(tcnq)_2][ClO_4]_2$, which exhibits an isotropic e.s.r. signal, g = 2.05, and $\mu_{eff.}$ = 1.88 μ_B. Reaction of the five-co-ordinate $[Ni(dmpae)_2X]ClO_4$ [dmpae = 1,2-bis(methylphenylarsino)ethane] with tcne yields either $[Ni(dmpae)(tcne)X]ClO_4$ (X = Cl or NCS) or $[Ni(dmpae)_2(tcne)_2]X[ClO_4]$ (X = Cl, Br, or I). Both of these types of complexes are six-co-ordinate and contain *N*-bonded unidentate neutral tcne ligands. We have obtained no evidence for olefinic bonding in any of these complexes.

WHEREAS no simple olefin complexes of nickel(II) have been isolated several reactive complexes have been reported for nickel(0).[1] We have, however, previously shown that relatively ' hard ' acceptor atoms such as nickel(II) may be persuaded to co-ordinate an olefinic group when the olefin is part of a multidentate ligand such as (but-3-enyl)bis(3-dimethylarsinopropyl)arsine, L.[2] For example, the five-co-ordinate [Ni(L)X]Y (X = Cl or Br; Y = Cl, Br, or ClO_4) complexes contain co-ordinated olefin, as evidenced by electronic and i.r. spectra. It is significant however, that a similar diarsine–diolefin, $As(CH_2CH_2CH{=}CH_2)_2(CH_2CH_2CH_2AsMe_2)$, L′, forms only $[Ni(L')_2X]^+$ (X = Cl, Br, or I) complexes which contain only nickel–arsenic co-ordinate bonds.[2] We concluded from these reactions that the promotion of nickel–olefin co-ordination with L, but not L′, was due to the presence of two arsine donors in the plane of the molecule which modifies the relatively ' hard ' nickel(II) acid. The chelate effect appears to be of less importance, otherwise at least one olefin donor might have been expected to co-ordinate in L′ complexes.

We thus decided to study the reactions of nickel(II) complexes containing arsine ligands with the electron-deficient olefins tetracyanoethylene (tcne) and 7,7,8,8-tetracyanoquinodimethane (tcnq), in the hope of synthesising novel complexes having an η^2-olefinic bond to the nickel(II) atom. In this we were disappointed, but isolated instead new complexes in which the tcne and tcnq ligands are bonded to nickel *via* the cyano-groups.

RESULTS AND DISCUSSION

The chelating arsine ligands used in this study were bis(3-dimethylarsinopropyl)phenylarsine, bdpa,[3] and 1,2-bis(methylphenylarsino)ethane, dmpae.[4] The dimeric five-co-ordinate complex $[Ni_2(bdpa)_3(H_2O)][ClO_4]_4$, the monomeric five-co-ordinate complex $[Ni(dmpae)_2X]$-

TABLE 1

Analytical data for the nickel–arsine–tcne/tcnq complexes

Compound	Colour	Analysis (%) [a]					Λ [b]/ S cm² mol⁻¹	$\mu_{eff.}$ [c]
		C	H	N	Cl [a]	Ni		
$[Ni_2(bdpa)_2(tcne)][ClO_4]_2$	Orange	34.3(34.1)	4.4(4.4)	4.3(4.2)	5.6(5.3)	8.5(8.8)	153	
$[Ni_2(bdpa)_2(tcne)][BPh_4]_2$	Orange	57.8(58.2)	5.8(5.6)	3.5(3.2)		6.4(6.6)	167	
$[Ni_2(bdpa)_2(tcne)][PF_6]_2$	Orange	31.8(32.0)	4.0(4.1)	3.7(3.9)		8.0(8.2)	160	
$[Ni_2(bdpa)_2(tcnq)][ClO_4]_2$	Brown	37.6(37.4)	4.3(4.4)	4.3(4.0)	5.4(5.0)	8.0(8.3)	157	
$[Ni_2(bdpa)_2(tcnq)][BPh_4]_2$	Brown	59.5(59.7)	5.6(5.5)	3.3(3.0)		6.3(6.4)	165	
$[Ni(bdpa)(tcnq)]ClO_4$	Purple	41.5(41.6)	4.3(4.1)	7.3(6.9)	4.7(4.4)	7.0(7.3)	95 [d]	
$[Ni(dmpae)_2(tcne)Cl]ClO_4$	Reddish brown	40.6(43.6)	3.5(3.8)	5.6(5.4)	6.6(6.8)	5.2(5.6)		
$[Ni(dmpae)_2(tcne)_2]Cl[ClO_4]$	Dark brown	43.8(44.9)	3.4(3.4)	9.7(9.5)	6.4(6.0)	4.7(5.0)		2.87
$[Ni(dmpae)_2(tcne)(NCS)]ClO_4$	Reddish brown	41.8(43.8)	4.5(3.7)	5.8(6.6)	3.8(3.4)	6.0(5.5)		
$[Ni(dmpae)_2(tcne)_2][NCS][ClO_4]$	Dark brown	44.5(45.1)	3.3(3.3)	10.9(10.5)	2.8(3.0)	4.8(4.9)		2.88
$[Ni(dmpae)_2(tcne)_2]Br[ClO_4]$	Reddish brown	41.8(43.3)	3.1(3.3)	9.1(9.2)		4.9(4.8)		2.90
$[Ni(dmpae)_2(tcne)_2]I[ClO_4]$	Dark green	41.0(41.7)	3.0(3.2)	9.1(8.8)		4.4(4.7)		2.80
$[Ni(dmpae)_2(tcne)_2][ClO_4]_2$	Dark green	41.9(42.7)	3.3(3.2)	8.6(9.1)	5.3(5.7)	4.6(4.8)		2.80

[a] Calculated values are given in parentheses. [b] In 10^{-3} mol dm^{-3} nitromethane. [c] μ_B. [d] Decomposes rapidly.

TABLE 2

Infrared spectroscopic data (cm^{-1}) of tcne and related complexes

Compound	$\nu(C\equiv N)$	$\nu(C=C)$	Ref.
tcne	2 260s, 2 228m	1 570	8
$tcne^{\bullet -}$	2 200s, 2 183m	1 360	8
$tcne^{2-}$	2 160s, 2 095m	1 260	8
$[(Ph_3P)_2(OC)Ir{-}hcbd{-}Ir(CO)(PPh_3)_2]$	2 207w, 2 196 (sh), 2 181vs, 2 147vs, 2 136vs, 2 122 (sh)	1 346w, 1 295vs, 1 273m, 1 260 (sh)	9
$[(Ph_3P)_2(OC)Rh{-}hcbd{-}Rh(CO)(PPh_3)_2]$	2 208w, 2 195 (sh), 2 181vs, 2 170 (sh), 2 141s, 2 130 (sh)	1 344w, 1 296vs, 1 208 (sh)	9
$[(Ph_3P)_2(OC)Ir{-}tcne{-}Ir(CO)(PPh_3)_2]$	2 175s, 2 098vs	1 256m	9
[(py)(acacen)Co–tcne–Co(acacen)(py)] (green)	2 241w, 2 190s, 2 180 (sh), 2 152s, 2 108 (sh)		36
(purple)	2 248w, 2 202s, 2 180s, 2 170s, 2 158 (sh), 2 120s		36
$[\{Co(acacen)(tcne)\}_n]$	2 235w, 2 212s, 2 180 (sh), 2 135 (sh)		36
$[Ni_2(bdpa)_2(tcne)][ClO_4]_2$	2 160s, 2 120w, 2 100s	1 260m	
$[Ni_2(bdpa)_2(tcne)][BPh_4]_2$	2 160vs, 2 100s	1 260m	
$[Ni_2(bdpa)_2(tcne)][PF_6]_2$	2 160vs, 2 100s	1 260m	
$[Ni(dmpae)_2(tcne)Cl]ClO_4$	2 240w, 2 216s, 2 140w		
$[Ni(dmpae)_2(tcne)_2]Cl[ClO_4]$	2 240w, 2 210s, 2 180w, 2 140w		
$[Ni(dmpae)_2(tcne)(NCS)]ClO_4$	2 240w, 2 215s, 2 142w		
$[Ni(dmpae)_2(tcne)_2][NCS][ClO_4]$	2 240w, 2 220s, 2 186 (sh), 2 140w		
$[Ni(dmpae)_2(tcne)_2]Br[ClO_4]$	2 240w, 2 210s, 2 180 (sh), 2 140w		
$[Ni(dmpae)_2(tcne)_2]I[ClO_4]$	2 240w, 2 220s, 2 183 (sh), 2 143w		
$[Ni(dmpae)_2(tcne)_2][ClO_4]_2$	2 240w, 2 210s, 2 180w, 2 140w		

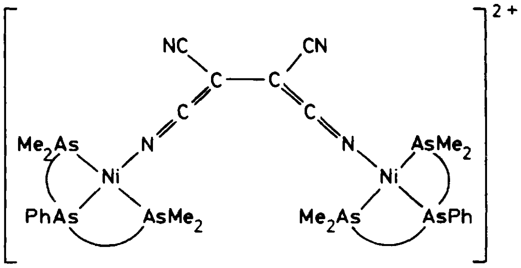
ClO_4, and planar $[Ni(dmpae)_2][ClO_4]_2$ [5] were synthesised as previously described.

A purple solution of $[Ni_2(bdpa)_3(H_2O)][ClO_4]_4$ in refluxing dichloromethane yielded bright orange $[Ni_2(bdpa)_2(tcne)][ClO_4]_2$ on reaction with tcne. This complex is soluble in a wide variety of polar and non-polar solvents, from which it can be recovered without decomposition. Reaction with $NaBPh_4$ or $[NH_4][PF_6]$ in a 1 : 4 ratio in methanol yielded $[Ni_2(bdpa)_2(tcne)]Y_2$ ($Y = BPh_4$ or PF_6), Table 1. The electronic spectra in the solid state and in dichloromethane are similar and are characterised by a broad strong absorption at *ca.* 23 800 cm^{-1}, assignable to the $d_{xy} \rightarrow d_{x^2-y^2}$ transition in square-planar complexes.[6] All the complexes are diamagnetic and in nitromethane solution have molar conductivities characteristic of 1 : 2 electrolytes,[7] Table 1.

Sensitive probes for determining the nature of complexed tcne are the $\nu(C\equiv N)$ and $\nu(C=C)$ regions of the i.r. spectrum.[8-11] Table 2 illustrates well how the tcne, $tcne^{\bullet -}$, and $tcne^{2-}$ species may be distinguished. All of the three products, $[Ni_2(bdpa)_2(tcne)]Y_2$ ($Y = ClO_4$, BPh_4, or PF_6), exhibit two $\nu(C\equiv N)$ bands and one $\nu(C=C)$ band in the region indicative of the dianion $tcne^{2-}$. Fundamental absorptions at 1 080 ($Y = ClO_4$), 1 580 ($Y = BPh_4$), and 840 cm^{-1} ($Y = PF_6$) characteristic of the counter ions were also observed, and there was no overlap between bands assignable to the bdpa ligand and $tcne^{2-}$.

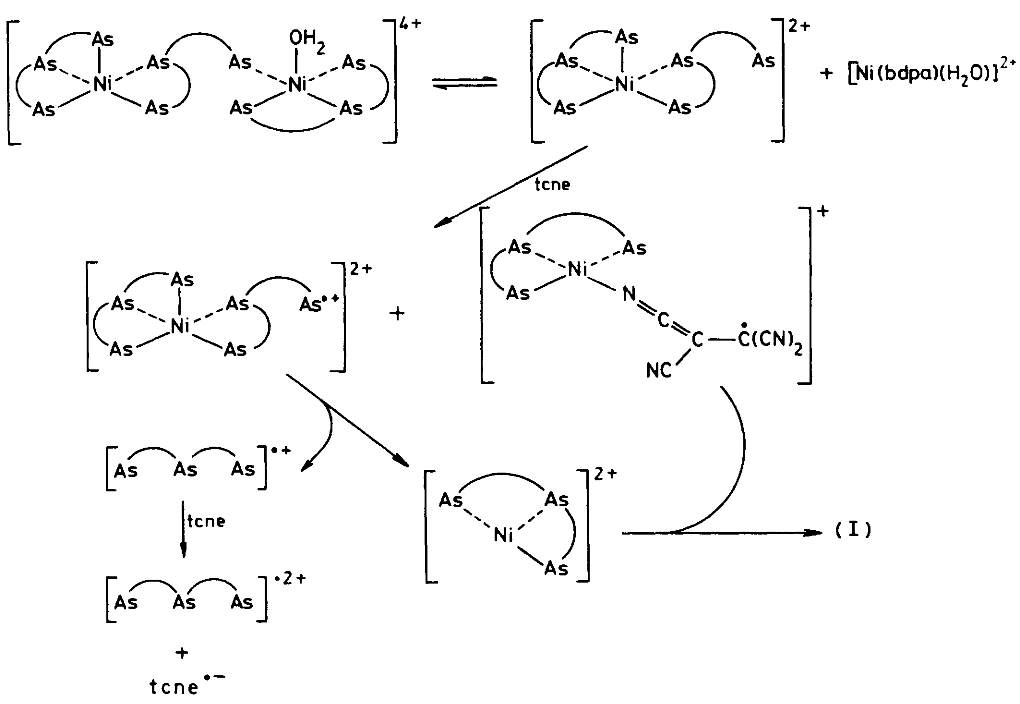
Thus, for the complexes $[Ni_2(bdpa)_2(tcne)]Y_2$ two structures may be assigned, where the $tcne^{2-}$ is co-ordinated to the nickel atom by two nitrile groups in a *cis*, (I), or *trans* configuration. Recently, Beck *et al.*[9] have prepared $[(Ph_3P)_2(OC)Ir{-}tcne{-}Ir(CO)(PPh_3)_2]$ from Vaska's complex and $tcne^{\bullet -}$. On the basis of a dipole-moment study this was assigned a *cis*-bridging structure. The reaction of $[Rh(CO)(PPh_3)_2Cl]$ with $tcne^{\bullet -}$ also yielded a binuclear complex $[(Ph_3P)_2(OC)Rh{-}hcbd{-}Rh(CO)(PPh_3)_2]$ [hcbd = 1,1,2,3,4,4-hexacyanobutenediide, $(NC)_2CC(CN){=}C(CN)C(CN)_2{}^{2-}$], an *X*-ray crystal structure of which showed *trans*-bridging hcbd.[12] From Table 2 it can be seen that the i.r. spectra of $[Ni_2(bdpa)_2(tcne)]^{2+}$ are very similar to those of the *cis*-bridging complex of Beck *et al.*, and so we assign structure (I) to our species.

In the reactions of the rhodium and iridium complexes discussed above the tcne reagent is added to the mixture as $tcne^{\bullet -}$, but in our reactions it is added as the neutral compound, and is apparently reduced to $tcne^{\bullet -}$ *in situ.* It is known [13] that reactions of phosphines and arsines with tcne produce a high concentration of $tcne^{\bullet -}$. We thus propose the Scheme as a tentative reaction mechanism. There is evidence [14,15] that the initial disproportionation to form the five-co-ordinate $[Ni(bdpa)_2]^{2+}$ with one free arsine is quite possible, and this mechanism is quite similar in some respects to that proposed by Beck *et al.*,[9] drawn from previous observations by Webster *et al.*[16] and Paul *et al.*[17]



(I)

Differences in co-ordinating behaviour of tcne and 7,7,8,8-tetracyanoquinodimethane (tcnq) have been noted previously,[18-22] and so we have also employed the more electronegative tcnq in this study. Thus, if $[Ni_2(bdpa)_3(H_2O)][ClO_4]_4$ is made to react with tcnq in a 1 : 3 ratio the brown complex $[Ni_2(bdpa)_2(tcnq)][ClO_4]_2$ is obtained, which can subsequently yield $[Ni_2(bdpa)_2(tcnq)][BPh_4]_2$ by metathesis, Table 1. These complexes



SCHEME Groups on the bdpa ligand have been omitted for simplicity

are both diamagnetic and exhibit molar conductivities in nitromethane characteristic[7] of 1 : 2 electrolytes, Table 1. The electronic absorption spectra in the solid state and in dichloromethane are characteristic of planar species,[6] exhibiting maxima in the 18 000—24 000 cm^{-1} region.

Table 3 contains ν(C≡N) and ν(C=C) bands of tcnq,[23] the radical anion, Na(tcnq),[21] a gold(I) complex shown to contain the tcnq ligand as a radical anion,[24] and a tin(II) complex in which the tcnq radical anion bridges two tin atoms through the N atoms of the nitrile groups.[22] From this comparison it can be seen that the nitrile stretching frequencies which occur in the regions of 2 150—2 152 and 2 070—2 075 cm^{-1} in the nickel–bdpa complexes are considerably lower than those reported for the tcnq radical anion. Thus the radical anion appears not to be present in these complexes. This is also borne out by the observed diamagnetism and the lack of a strong e.s.r. signal expected for $tcnq^{\bullet -}$. In fact, the i.r. spectra are more consistent with the presence of tcnq as the dianion. It has been reported previously that reaction of $[Co(acacen)(py)_2]\cdot tcnq$ [acacen = *NN'*-ethylenebis(acetylacetoneiminate), py = pyridine], in which the tcnq is present as the radical anion, with [Co(acacen)(py)] in the presence of pyridine gives $[\{Co(acacen)(py)_2\}_2]\cdot tcnq$, containing the tcnq dianion.[18] In this complex the ν(C=C) band of $tcnq^{2-}$ is obscured by other absorptions,[18] but since $tcne^{\bullet -}$ and $tcnq^{2-}$ show similar shifts (198 and 212 cm^{-1} respectively) to that of the neutral species, then it may reasonably be expected that a shift for $tcne^{2-}$ (312 cm^{-1}) might be reflected in a band in the $tcnq^{2-}$ spectrum in the 1 230—1 200 cm^{-1} region. We observe a medium-intensity band at 1 220 cm^{-1} for the $[Ni_2(bdpa)_2(tcnq)]^{2+}$ complexes, Table 3, and so we assign the dianionic species to these complexes. It is difficult to envisage any structure for these $[Ni_2(bdpa)_2(tcnq)]^{2+}$ complexes other than the bridged dimer (II).

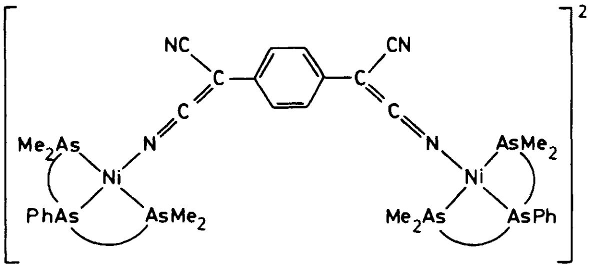
TABLE 3

Infrared spectroscopic data (cm^{-1}) of tcnq and related complexes

Compound	ν(C≡N)	ν(C=C)	Ref.
tcnq	2 220m	1 540m	23
Na(tcnq)	2 200m, 2 163m	1 330m	21
$[Au(PPh_3)_2]\cdot tcnq$	2 176m, 2 156m	1 328m	24
$[Sn(tcnq)_{1.5}(acac)_2]$ [a]	2 200w, 2 170m, 2 100s	*b*	22
$[Co(acacen)(py)_2]\cdot tcnq$	2 177m, 2 145m	1 330w	18
$[\{Co(acacen)(py)_2\}_2]\cdot tcnq$	2 151m, 2 102m	*b*	18
$[Ni_2(bdpa)_2(tcnq)][ClO_4]_2$	2 200w, 2 150m, 2 070s	1 220m	
$[Ni_2(bdpa)_2(tcnq)][BPh_4]_2$	2 200w, 2 152m, 2 075s	1 220m	
$[Ni(bdpa)(tcnq)]ClO_4$	2 160s, 2 100s	1 222m	

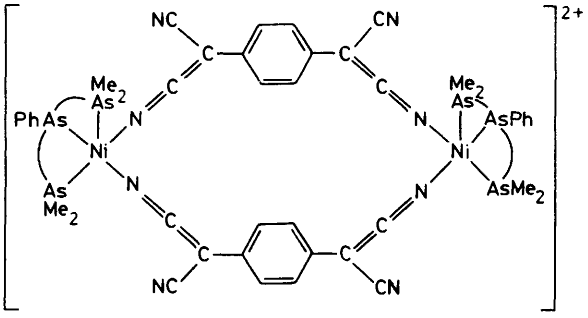
[a] acac = Acetylacetonate. [b] Obscured by ligand bands.

Like tcne, tcnq is readily reduced by arsines[25] and so the reaction of tcnq with $[Ni_2(bdpa)_3(H_2O)][ClO_4]_4$ probably occurs as in the Scheme.



(II)

The reaction of $[Ni_2(bdpa)_3(H_2O)][ClO_4]_4$ with tcnq in a ratio much greater than 1 : 3 under rigorously deoxygenated conditions results in the formation and isolation of $[Ni(bdpa)(tcnq)]ClO_4$; this complex may also be isolated from the reaction of $[Ni_2(bdpa)_2(tcnq)][ClO_4]_2$ and tcnq (see Experimental section). This pale purple solid exhibits the usual unsplit strong band at 1 080 cm^{-1} in the i.r. spectrum, assignable to unco-ordinated perchlorate.[26] Strong bands at 2 160 and 2 100 cm^{-1} in the $\nu(C{\equiv}N)$ region, and a band at 1 222 cm^{-1}, assignable to $\nu(C{=}C)$, all suggest the presence of the $tcnq^{2-}$ dianion. The electronic absorption spectrum of this complex exhibits a very intense broad asymmetric absorption with a maximum at 20 800 cm^{-1} and a shoulder at 16 100 cm^{-1}. This profile is characteristic of five-co-ordinate nickel(III) species as is the room-temperature magnetic moment of 1.88 μ_B.[27] Further evidence for a d^7 nickel(III) species is obtained from the e.s.r. data of a powdered sample. At room temperature no signal is observed, but at 133 K a very broad, apparently isotropic signal with $g = 2.05$ and linewidth *ca.* 1 100 G* was observed, together with a very weak, sharp signal at $g = 2.003$ and with linewidth *ca.* 15 G. The latter signal is attributed to a very small amount of $tcnq^{\bullet -}$ as an impurity. Very few e.s.r. spectra of nickel(III) complexes have been reported, but those which have been obtained [27-30] indicate that the g value of the $tcnq^{2-}$ complex is consistent with a nickel(III) species. The proposed structure is shown in (III).



(III)

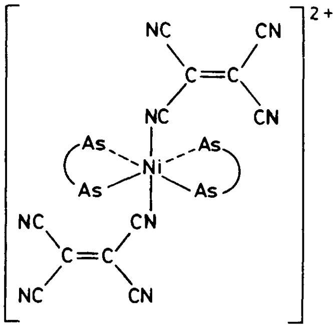
The formation of (III) is probably due to the fact that tcnq is a powerful oxidising agent and that planar nickel(II) chelates are known to undergo one-electron oxidations.[31-33] The square-planar dimer with a single bridging $tcnq^{2-}$ ligand thus reacts as in equation (1).

$$[Ni_2(bdpa)_2(tcnq)][ClO_4]_2 + tcnq \longrightarrow [Ni_2(bdpa)_2(tcnq)_2][ClO_4]_2 \quad (1)$$

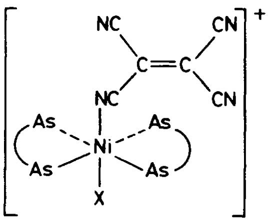
When either $[Ni_2(bdpa)_2(tcnq)][ClO_4]_2$ or $[Ni_2(bdpa)_2(tcnq)_2][ClO_4]_2$ is dissolved in nitromethane or other polar solvents the solutions become bright orange exhibiting a strong absorption in the visible region at 20 964 cm^{-1} with a shoulder at 26 109 cm^{-1}. It has been shown that admission of dioxygen to an electrochemical cell containing $tcnq^{2-}$ results in the formation of a bright orange solution absorbing at 20 964 and 26 315 (sh) cm^{-1},[34,35] the $tcnq^{2-}$ having been oxidised to the $tcnq^{\bullet -}$ carbanion. Our observations thus give further evidence for the existence of the $tcnq^{2-}$ dianion in the nickel(II) and nickel(III) complexes originally.

We carried out further reactions between the five-co-ordinate square-pyramidal complexes $[Ni(dmpae)_2X]ClO_4$ and tcne. The complexes isolated, Table 1, are formulated as $[Ni(dmpae)_2(tcne)X]ClO_4$ (X = Cl or NCS) and $[Ni(dmpae)_2(tcne)_2]X[ClO_4]$ (X = Cl, Br, I, NCS, or ClO_4).† The i.r. spectra of these complexes are listed in Table 2 and may be compared with tcne in other complexes.[8,9,36] The spectra in the $\nu(C{=}N)$ region of all the compounds are complex, but similar (those with only one tcne ligand are slightly less complex), and the lowered symmetry [11] is accompanied by a shift to lower energy. The spectra are comparable to those in the Co–acacen complexes of Crumbliss and Basolo [36] in which the tcne ligand is co-ordinated as the neutral molecule through one nitrogen donor. We are unable to assign any i.r. band due to $\nu(C{=}C)$. For $[Ni(dmpae)_2(tcne)(NCS)]ClO_4$ and $[Ni(dmpae)_2(tcne)_2][NCS][ClO_4]$ strong absorptions appear at 2 080 and 2 048 cm^{-1}, assignable to *N*-bonded and free thiocyanate ion respectively.[37]

The insolubility of the complexes prevented solution studies, but both the room-temperature magnetic moments, Table 1, and the electronic reflectance spectra are indicative of octahedral nickel(II) species. The reflectance spectra of $[Ni(dmpae)_2(tcne)_2]^{2+}$ are identical (bands at 9 700, 14 600, and 21 300 cm^{-1}) and those of $[Ni(dmpae)_2(tcne)X]^+$ differ very slightly reflecting the change in the sixth ligand. The complexes are thus assigned structures (IV) and (V) respectively.



(IV)



(V)

When the nickel(II) complexes were suspended in polar solvents such as nitromethane, very weak e.s.r. signals, $g = 2.0027$, attributable to $tcne^{\bullet -}$ were obtained, indicating decomposition. We have also shown that

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* Throughout this paper: 1 G = 10^{-4} T.

† A referee has pointed out that a few of the dmpae complexes have poor analyses. We have no explanation for this since we can detect no obvious impurities. We also point out that the low observed magnetic moments for the six-co-ordinate complexes are in line with the other relatively rare examples of this geometry for heavy donor atoms (see W. Levason, C. A. McAuliffe, and S. M. Nelson, *Inorg. Chim. Acta*, 1976, **18**, L5 and refs. therein).

tcne$^{\bullet -}$ may be generated by mixing free dmpae ligand and tcne in an e.s.r. tube. An intense spectrum of the radical anion, $g = 2.0027$ (11 lines with a spacing of 1.56 G), is seen, similar to that reported by LeBlanc.[38]

In conclusion we point out that in no case have we observed co-ordination of the double bond in the tcne and tcnq olefins, but this work has produced complexes which contain examples of neutral tcne, dianionic tcne^{2-}, and dianionic tcnq^{2-}, reflecting the sensitivity of these olefins to the nature of the acceptor complex.

EXPERIMENTAL

Infrared and u.v.–visible spectra were recorded on a Perkin-Elmer spectrophotometer model 621, and a Beckman Acta mark IV spectrophotometer respectively. E.s.r. spectra were determined using a Varian E-9 spectrometer operating in the '*X*-band' frequency using a 10 kHz modulation, and a Varian E-257 accessory for variable-temperature measurements. Conductivities were measured at 20 °C on a Cambridge Instruments conductivity bridge, and magnetic susceptibilities were determined on a Newport magnetic balance using mercury tetrathiocyanatocobaltate(II) as a calibrant.

Reactions of Tetracyanoethylene.—(*a*) *With* $[Ni_2(bdpa)_3(H_2O)][ClO_4]_4$. When a stirred solution of tcne (0.19 g, 1.5 mmol) and the nickel complex (0.94 g, 0.5 mmol) in dichloromethane (50 cm^3) was heated under reflux for 2 h the violet colour changed to deep orange. Removal of the solvent gave an orange oil, which was taken up in a small amount of fresh dichloromethane and cyclohexane was added slowly with rapid stirring to give $[Ni_2(bdpa)_2(tcne)][ClO_4]_2$ (0.47 g, 0.35 mmol, 70%) as an amorphous *powder*, m.p. 182—184 °C (decomp.).

Dropwise addition of a methanolic solution of sodium tetraphenylborate (0.40 g, 1.20 mmol) to a rapidly stirred solution of $[Ni_2(bdpa)_2(tcne)][ClO_4]_2$ (0.40 g, 0.30 mmol) in the same solvent under a nitrogen atmosphere gave an orange-brown *precipitate* of $[Ni_2(bdpa)_2(tcne)][BPh_4]_2$ (0.44 g, 0.25 mmol, 83%), m.p. 124—126 °C (decomp.), which was recrystallised from a mixture of dichloromethane and methanol.

Under similar conditions, reaction between ammonium hexafluorophosphate (0.20 g, 1.22 mmol) and $[Ni_2(bdpa)_2(tcne)][ClO_4]_2$ (0.40 g, 0.30 mmol) gave $[Ni_2(bdpa)_2(tcne)][PF_6]_2$ (0.36 g, 0.26 mmol, 87%), m.p. 130 °C (decomp.).

(*b*) *With* $[Ni(dmpae)_2Cl]ClO_4$. A mixture of tcne (0.13 g, 1.0 mmol) and $[Ni(dmpae)_2Cl]ClO_4$ (0.46 g, 0.5 mmol) in dichloromethane (20 cm^3) was heated under reflux with stirring for 30 min. Removal of most of the solvent and addition of an equal volume of cyclohexane precipitated $[Ni(dmpae)_2(tcne)Cl]ClO_4$ (0.40 g, 0.38 mmol, 76%), m.p. 140—145 °C (decomp.).

When this reaction was repeated, but the mixture was refluxed for 24 h, the product was $[Ni(dmpae)_2(tcne)_2]Cl[ClO_4]$ (0.40 g, 0.34 mmol, 74%), m.p. 184—185 °C (decomp.).

(*c*) *With* $[Ni(dmpae)_2(NCS)]ClO_4$. A solution of tcne (0.13 g, 1.0 mmol) and $[Ni(dmpae)_2(NCS)]ClO_4$ (0.47 g, 0.5 mmol) in dichloromethane was refluxed with stirring for 30 min to give $[Ni(dmpae)_2(tcne)(NCS)]ClO_4$ (0.40 g, 0.37 mmol, 74%), m.p. 110—120 °C (decomp.), after concentration of the solution and addition of cyclohexane.

When the reflux period was extended to 24 h a similar mixture gave $[Ni(dmpae)_2(tcne)_2][NCS][ClO_4]$ (0.48 g, 0.40 mmol, 80%), m.p. 130—132 °C (decomp.).

(*d*) *With* $[Ni(dmpae)_2Br]ClO_4$. Gentle reflux for 30 min of a solution of tcne (0.13 g, 1.0 mmol) and $[Ni(dmpae)_2Br]ClO_4$ (0.48 g, 0.5 mmol) in dichloromethane gave a *precipitate* of $[Ni(dmpae)_2(tcne)_2]Br[ClO_4]$ (0.52 g, 0.43 mmol, 86%), m.p. 120—128 °C (decomp.), which was washed in dry dichloromethane and dried *in vacuo*.

(*e*) *With* $[Ni(dmpae)_2I]ClO_4$. Under similar conditions, tcne (0.13 g, 1.0 mmol) and $[Ni(dmpae)_2I]ClO_4$ (0.50 g, 0.5 mmol) gave $[Ni(dmpae)_2(tcne)_2]I[ClO_4]$ (0.48 g, 0.38 mmol, 76%), m.p. 202—210 °C (decomp.).

(*f*) *With* $[Ni(dmpae)_2][ClO_4]_2$. When a solution of tcne (0.13 g, 1.0 mmol) and $[Ni(dmpae)_2][ClO_4]_2$ (0.49 g, 0.5 mmol) in dichloromethane (20 cm^3) was heated under gentle reflux with stirring for 48 h a *precipitate* of $[Ni(dmpae)_2(tcne)_2][ClO_4]_2$ (0.25 g, 0.20 mmol, 40%), m.p. 147—152 °C, was formed.

Reaction of 7,7,8,8-*Tetracyanoquinodimethane* (tcnq) *with* $[Ni_2(bdpa)_3(H_2O)][ClO_4]_4$.—A violet solution of tcnq (0.30 g, 1.50 mmol) and $[Ni_2(bdpa)_3(H_2O)][ClO_4]_4$ (0.94 g, 0.5 mmol) in dichloromethane (50 cm^3) turned orange on stirring under gentle reflux for 2 h. Removal of the solvent and recrystallisation of the residue from a mixture of dichloromethane and methanol gave $[Ni_2(bdpa)_2(tcnq)][ClO_4]_2$ (0.6 g, 0.42 mmol, 84%), m.p. 216—220 °C (decomp.).

When a large excess of tcnq (0.8 g, 3.9 mmol) and $[Ni_2(bdpa)_3(H_2O)][ClO_4]_2$ (0.8 g, 0.43 mmol) in dichloromethane (20 cm^3) was heated at reflux temperature for 48 h an orange-brown solution was formed. On standing at room temperature, this gradually turned to light purple, and on removal of the solvent, $[Ni(bdpa)(tcnq)][ClO_4]$ (0.48 g, 0.59 mmol, 69%), m.p. 200 °C (decomp.), precipitated. This was washed with dichloromethane and dried *in vacuo*.

Reactions of $[Ni_2(bdpa)_2(tcnq)][ClO_4]_2$.—(*a*) *With* tcnq. A mixture of tcnq (0.11 g, 0.54 mmol) and $[Ni_2(bdpa)_2(tcnq)][ClO_4]_2$ (0.2 g, 0.14 mmol) in dichloromethane (20 cm^3) stirred and heated under reflux for 12 h gave a pale purple precipitate of $[Ni(bdpa)(tcnq)]ClO_4$ (0.15 g, 0.19 mmol, 68%) which was identical to that described in the previous experiment.

(*b*) *With sodium tetraphenylborate*. Dropwise addition of a methanolic solution of sodium tetraphenylborate (0.4 g, 1.2 mmol) to a stirred solution of the nickel complex (0.42 g, 0.3 mmol) in the same solvent gave $[Ni_2(bdpa)_2(tcnq)][BPh_4]_2$ (0.5 g, 0.27 mmol, 90%), m.p. 198—201 °C (decomp.).

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