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Cyclidene complexes with bulky substituents

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Unbridged Ni(II) cyclidene complexes have been prepared with bulky substituents at the terminal nitrogen atoms (R^2 = $-C(Me)_2CH_2N(Me)_2$; $-CH(Ph)_2$; $-CH_2C(Me)_3$; $-CH_2CH(Ph)_2$) (substituent R^3 at the adjoining carbon = Me). Complexes containing the last two substituents and bridged with m-xylylene and $(CH_2)_6$ have also been synthesised. The effects of the bulky substituents on ^{13}C n.m.r spectra, electrochemical behaviour and oxygen binding ability are examined. The crystal structures of the m -xylylene-bridged complexes with $R^2 = CH_2C(Me)_3$, R^3 = Me (I) and R^2 = Me, R^3 = Ph (II) have been determined; both are monoclinic, $P2_1/c$, with (I) a = 13.463(1); b = 14.506(2); c = 26.72492)A, $\beta = 91.45(1)$, R = 0.082 for 3895 observed ($I/\sigma(I)> = 2.0$) reflections; (II) a = 24.721(6), b = 10.934(3), c = 16.321(5)Å, $\beta = 97.30(2)°$, R = 0.074 for 2992 observed ($I/\sigma(I)> = 3.0$) reflections

INTRODUCTION

Bridged cyclidene complexes form a family of molecules with remarkable potential for binding to additional species, including small ligand molecules, such as O_2 and CO,[1] and organic guest molecules, the latter by hydrophobic interactions.[2] Their chemical properties and reactions are controlled by the natures of the metal ion, the bridge, and the various substituent groups.[1e,1f,3] Our recent work has concentrated on the effect of bridge length[4] on, for example, dioxygen affinity, and on the contrast between large rigid cavities and smaller flexible ones.[4a,4e,5]

The substituent at position R^3 has also been varied with groups having greatly differing steric requirements, including H, Me, t-Bu, Ph, MeOPh.[6] Less attention has been given to variations in the substituent on the nitrogen atom, R^2, which has typically been Me or hydrogen, although a benzyl derivative has also been characterised crystallographically.[6] In this paper we examine the effects of substantially increasing the steric bulk of R^2 on the stabilities and dioxygen affinities of the cyclidene complexes. Surprisingly, the bulkiest groups cause undesirable changes in reactivity, while those with slightly smaller steric demands have little effect on molecular properties. It is consistent with these observations, that the crystal structure of the complex with R^2 = neo-pentyl shows only minor differences from those of other m-xylylene-bridged complexes.

RESULTS AND DISCUSSION

Syntheses.—The two most bulky groups examined in this work are—$C(Me)_2CH_2N(Me)_2$ and $-CH(Ph)_2$. Simple measures of steric bulk rank the t-butyl and related groups with tertiary carbons as quite high.[7] $-C(Me)_2CH_2N(Me)_2$ contains such a tertiary carbon. The unbridged Ni(II) cyclidene complexes for both substituents (compounds **1a, 1b**) were synthesized by well established procedures (**Scheme**),[8] as gold-colored compounds which were characterised primarily by ^{13}C N.M.R. However, the bridging reactions (step **C, Scheme**) with m-$BrCH_2C_6H_4CH_2Br$ (**1a**) or $TsO(CH_2)_6OTs$ (**1b**) failed to produce any isolable products; **1b** was also unreactive toward methyl iodide. In contrast, bulky groups having primary α-carbon atoms ($-CH_2C(Me)_3$ and—$CH_2CH(Ph)_2$) readily underwent the ring-closure reactions. Thus the unbridged complexes (**1c, 1d**) were converted to the m-xylylene- (**2a, 2b**) and hexamethylene-bridged (**2c**) cyclidenes. The latter two complexes were also demetallated to give the ligand salts (**3a, 3b**) and converted to the Co(II) complexes (**4a, 4b**) without

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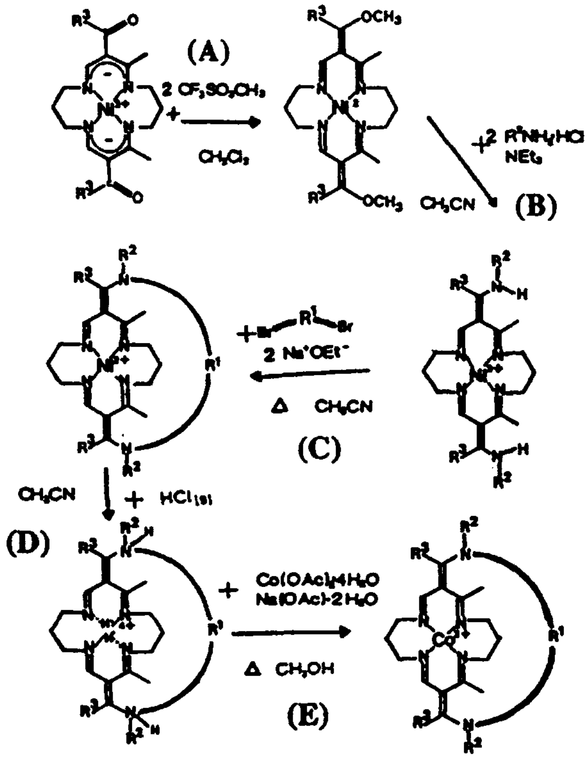

1a R^3 = Me $R^2 = C(Me)_2CH_2N(Me)_2$
1b R^3 = Me $R^2 = CH(Ph)_2$
1c R^3 = Me $R^2 = CH_2C(Me)_3$
1d R^3 = Me $R^2 = CH_2CH(Ph)_2$
2a R^3 = Me $R^2 = CH_2C(Me)_3$ $R^1 = CH_2$(m-C_6H_4)CH_2
2b R^3 = Me $R^2 = CH_2CH(Ph)_2$ $R^1 = CH_2$(m-C_6H_4)CH_2
2c R^3 = Me $R^2 = CH_2CH(Ph)_2$ $R^1 = (CH_2)_6$
2d R^3 = Ph R^2 = Me $R^1 = CH_2$(m-C_6H_4)CH_2
3a, 4a: substituents as **2b**
3b, 4b: substituents as **2c**

difficulty (not attempted for 2a). It is notable that the neo-pentyl group has a considerably larger Taft steric substituent constant[8] than even t-butyl (-1.74 vs. -1.54). Apparently, the key factor controlling the success of the bridging reaction is steric bulk immediately adjacent to the nitrogen atom, and, under normal reaction conditions, the bridging reaction proceeds reliably with a primary carbon at the α-position.

^{13}C N.M.R. spectra.—The ^{13}C N.M.R. spectra of complexes **1a-d** and **2a-c** are given in **Table 1** with full assignments (atoms identified in **Figure 1**). Three aspects of these spectra are notable. Comparison of the ^{13}C N.M.R. spectra of these complexes with those not having bulky groups (e.g. **2b** with the complex (except for the added or subtracted components).[9] Conversion of unbridged to bridged complexes has little effect on the spectra, except for the peaks assigned to the α-carbons of R^2 [unbridged (**1c** to **2a**) and bridged (**1d** to **2b**, **2c**)]. These resonances move downfield by 5-12 ppm, probably due to strain at the corresponding atoms. Additional evidence for steric effects at this position is seen in the spectra of **2b** and **2c**. In contrast to the simple spectrum for the R^2 atoms in **1d**, the bridged complexes show doublets for the phenyl carbon atoms (**q-t**), indicating the loss of free rotation about the CH_2-CH bonds.

Electrochemical Measurements.—The $E_{1/2}$ values for the Ni(II)/Ni(III) couple were obtained for the unbridged and bridged complexes **1c** and **2a** (listed with comparative data in **Table 2**).[3c,4a,10] The electrochemical behaviour for the unbridged species shows one surprising feature, its reversibility; these species are usually oxidized irreversibly.[11] The $E_{1/2}$ value for the unbridged complex (**1c**) is close to the values for the bridged complexes with R^2 = n-C_4H_9 or CH_3, as would be expected with an electron-donating group present (neo-pentyl). However, the results for **2a** show that bridging the sterically hindered complex produces a significant increase in $E_{1/2}$.

K_{O2} MEASUREMENTS.—The steric effects which influence the Ni(II)/Ni(III) couple might also be expected to affect the O_2 binding ability of the corresponding cobalt(II) complexes.[1] Values of K_{O2} were determined for the complex **4b** at two temperatures in water in the presence of N-methyl imidazole (**Table 3**). The results

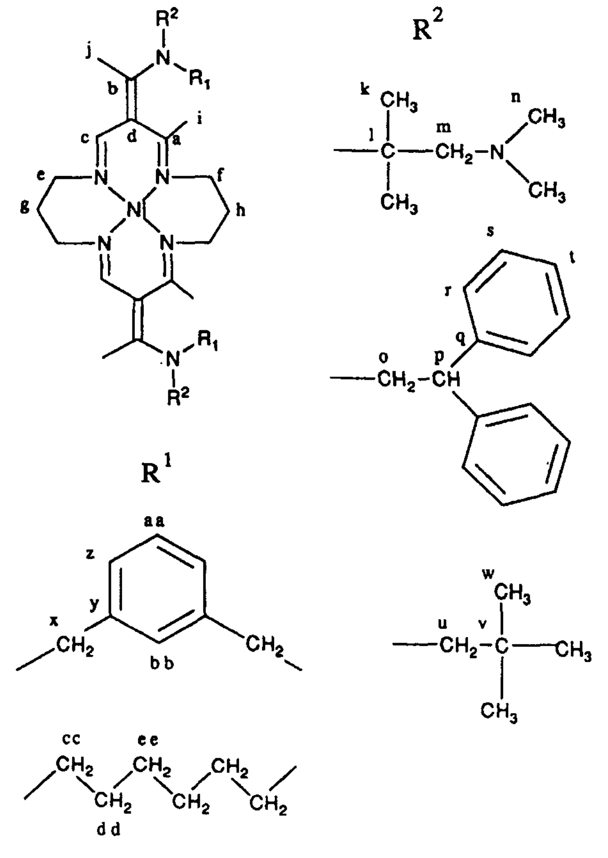

Figure 1 Atom labelling for bulky substituents.

Table 1 ^{13}C N.M.R. spectroscopic assignments (ppm relative to TMS, in CD_3CN) (R^3 = Me)

	A		*A*		*A*		
ligand	*Ia*	*Ib*	*Ic*	*Id*	*2a*	*2b*	*2c*
R^1	2H	2H	2H	2H	-mxyl-	-mxyl	-$(CH_2)_6$-
R^2	$C(Me)_2CH_2$ -$N(Me)_2$	$CH(Ph)_2$	$CH_2C(Me)_3$	$CH_2CH(Ph)_2$	$CH_2C(Me)_3$	$CH_2CH(Ph)_2$	$CH_2CH(Ph)_2$
a	168.13	167.46	169.20	167.60	173.98	173.49	168.59
b	161.55	168.99	168.15	168.63	167.58	167.63	171.29
c	160.15	161.01	160.27	160.28	159.97	159.83	160.95
d	116.71	112.95	112.44	112.42	114.11	114.22	111.78
e	56.53	56.53	56.31	56.47	56.66	56.68	55.03
f	51.81	51.66	51.49	51.70	52.24	51.83	51.18
g	28.55	30.07	30.09	30.08	29.71	29.68	30.10
h	30.41	30.40	30.47	30.71	30.41	30.25	30.24
i	21.46	21.38	21.43	20.49	20.48	20.72	20.10
j	17.50	16.84	15.65	15.52	22.13	20.40	19.01
k	28.55						
l	58.19						
m	70.91						
n	47.84						
o				50.03		60.19	55.78
p		64.13		51.57		52.10	51.11
q		141.05		142.22		142.32,142.24	142.23,142.19
r		130.23		129.25		130.19,129.97	129.94,129.85
s		128.59		129.02		129.01,129.00	129.58,129.01
t		129.41		128.29		128.54,128.34	128.67,128.21
u			56.76		68.07		
v			33.45		36.28		
w			27.38		28.12		
x					62.90		
y					138.21		
z					130.69		
aa					126.14		
bb					124.62		
cc							56.35
dd							25.65
ee							24.36

Note: the labelling of atoms e,f and g,h corresponds to that in ref. 5 but is reversed from that originally used (ref. 6)

Table 2 Electrochemical measurements (volts) ($R^3 = CH_3$)

Complex	R^2	R^1	*E*	E_p^c	E_p^a	ΔE_p*(mv)*	*ref.*
Ic	$CH_2CH(Me)_3$	2H	+0.81	+0.86	+0.75	111	a
2a	$CH_2C(Me)_3$	*m*-xyl	+0.85	+0.89	+0.81	84	a
	CH_2Ph	*m*-xyl	+0.82	+0.85	+0.77	70	b
	n-C_4H_9	*m*-xyl	+0.79	+0.82	+0.75	60	b
	CH_3	*m*-xyl	+0.78	+0.83	+0.74	70	b

a This work
b ref.6

Table 3 KO_2 Measurements (in H_2O) ($R^3 = CH_3$)

Complex	R^2	R^1	*T/°C*	*K/torr*$^{-1}$	*ref.*
4b	$CH_2CH(Ph)_2$	$(CH_2)_6$	1.0	3.1(2)	a
4b	$CH_2CH(Ph)_2$	$(CH_2)_6$	10.0	1.16(9)	a
	H	$(CH_2)_6$	1.6	2.76(6)	b
	CH_3	$(CH_2)_6$	10.0	4.5(4)	b
	CH_3	$(CH_2)_6$	19.7	1.6(1)	b

a This work
b *J.* Stevens, Ph. D. Thesis, The Ohio State University, 1979

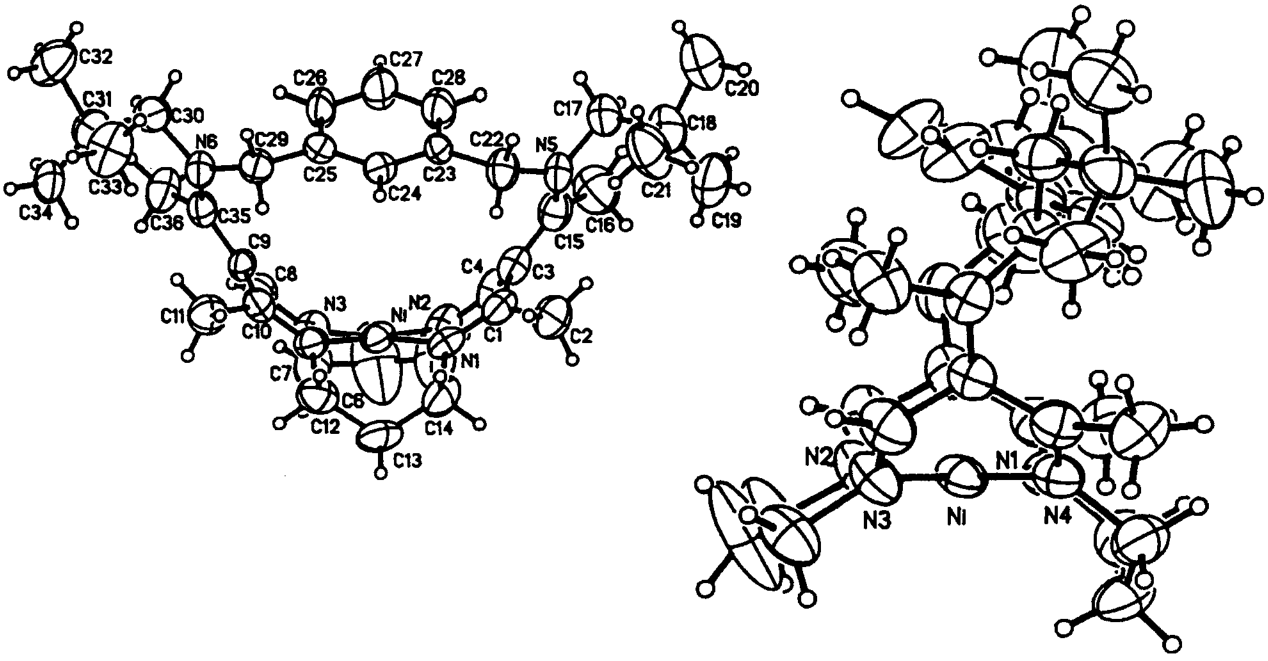

Figure 2 Two views of the crystal structure of **2a**, showing the numbering scheme.

are similar to, though rather smaller than, those for complexes with $R^2 = CH_3$ or H, indicating that the bulky R^2 group has little effect on dioxygen affinity.

Crystal structures.—The crystal structure of **2a** has been determined, to identify changes in geometry associated with the bulky R^2 groups; the results are compared with those for other m-xylylene bridged cyclidenes,[1d] in particular **2d** (previously unpublished) which has R^2 = Me, R^3 = Ph. **Figures 2** and **3** give views of **2a** and **2d**, and principal dimensions are compared in **Table 4. Figure 4** shows the standard parameters used in the characterization of lacunar cyclidenes.[4e,12]

The structure of **2a** has the expected overall geometry. The cavity width and height, measured respectively by the N_3N_3' and Ni-C(31) distances (7.26(2) and 4.02(1)Å), are similar to those in **2d** (7.30(2) and 3.98(2)Å) and in other m-xylylene-bridged cyclidenes, as would be expected for this rigid bridging group.

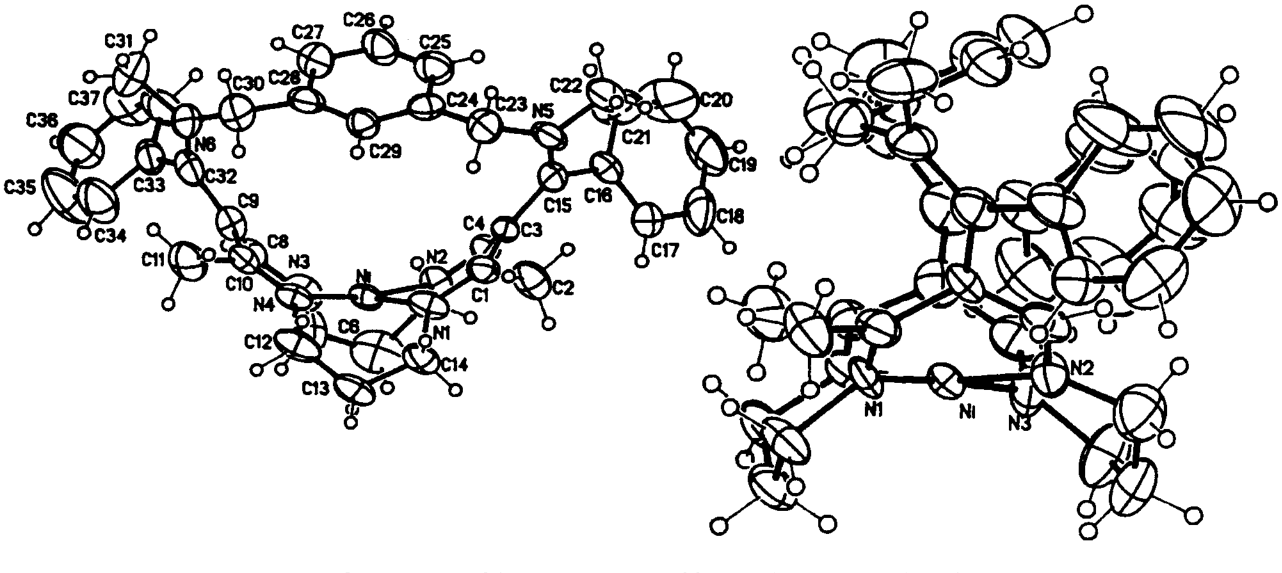

Figure 3 Two views of the crystal structure of **2d**, showing the numbering scheme.

Table 4 Selected dimensions (Å) and (°) for 2a and 2d

	(2a)	(2d)
Ni-N(1)	1.890(8)	1.865(8)
Ni-N(2)	1.878(9)	1.900(6)
Ni-N(3)	1.867(8)	1.878(8)
Ni-N(4)	1.881(8)	1.900(7)
N(1)-C(1)	1.30(2)	1.32(1)
C(1)-C(3)	1.43(2)	1.44(1)
C(3)-C(4)	1.44(2)	1.40(1)
C(4)-N(2)	1.28(2)	1.27(1)
N(3)-C(8)	1.28(1)	1.29(1)
C(8)-C(9)	1.43(1)	1.40(1)
C(9)-C(10)	1.44(1)	1.46(1)
C(10)-N(4)	1.30(1)	1.27(1)
C(3)-C(15)	1.41(2)	1.42(1)
C(9)-C(32)	-	1.40(1)
C(9)-C(35)	1.41(1)	-
C(15)-N(5)	1.32(1)	1.33(1)
N(6)-C(32)	-	1.36(1)
N(6)-C(35)	1.33(1)	-
N(5)-C(17)-C(18)	115.2(9)	-
N(6)-C(30)-C(31)	115.8(8)	-

Indeed, **2a** and **2d** have exceptionally similar cavity geometries (seen superimposed in **Fig. 5**), with an r.m.s. deviation between corresponding atoms of only 0.09Å (maximum deviation 0.20Å), for a least-squares fit excluding the saturated rings. The latter are somewhat different, because the atoms in the ring away from the cyclidene methyl groups in **2a** show high thermal motion, indicating oscillation between boat and chair forms (clearly visible in **Figs 2a – b**). Structure **2a** does show a specific steric effect in the large N-C-C angles within the neo-pentyl groups themselves (angles at C(19) and C(24) in **2a**, mean 116.5(1)).

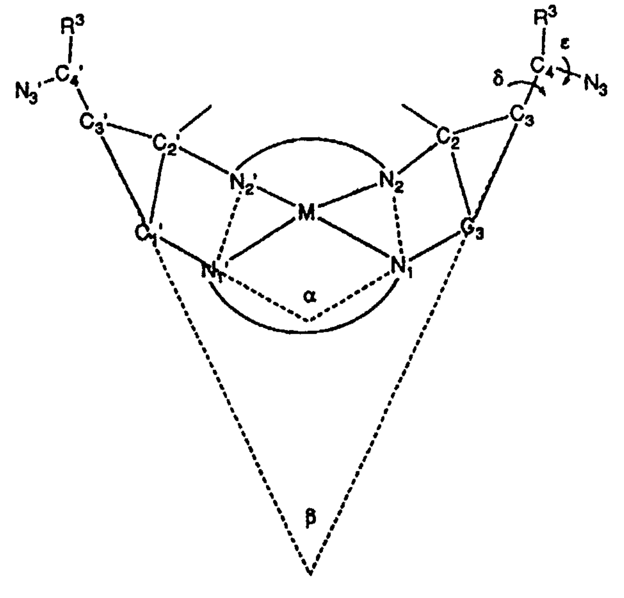

Figure 4 Standard dimensional parameters for cyclidenes. Subscripts are used for identifying atom labels (e.g. N_3).

The most significant difference between **2a** and **2d** lies in their R^3 groups; the phenyl groups of **2d** point more directly outwards from the cavity (78.4(1)° between C-C lines) than do the CH_3 groups of **2a** (64.1(1)°). This probably results from steric repulsion between the Me and neo-pentyl groups; the resulting untwisting of the C_3-C_4 bond leads to a mean dihedral angle (parameter δ) of 25(1)° in **2a**, compared to 34(1)° in **2d**, and 39° when $R^2 = R^3 =$ Me. This decrease in angle δ is predicted to increase the degree of conjugation in the unsaturated cyclidene system, as has been shown for a series of unbridged cyclidenes (although the precision of the present determinations are too low for the corresponding bond length changes to be seen).[12] These changes in conjugation must have electronic effects on the metal, and are probably therefore responsible for the unusual electrochemical properties found for **2a**.

Experimental

Physical Measurements.—Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee, or Schwarzkopf Microanalytical Laboratory, Woodside, New York.

^{1}H proton nuclear magnetic resonance spectra were recorded using either a Varian 360-L spectrometer which operated at 60 MHz or a Varian 390-L model which operated to 90 MHz. ^{13}C NMR spectra were recorded on a Bruker WP-80 Fourier transform instrument, operating at 20.1 MHz. Both broadband proton decoupled and off-resonance decoupling were routinely used for ^{13}C NMR samples. Chemical shifts in the ^{1}H and ^{13}C NMR spectra were assigned relative to TMS.

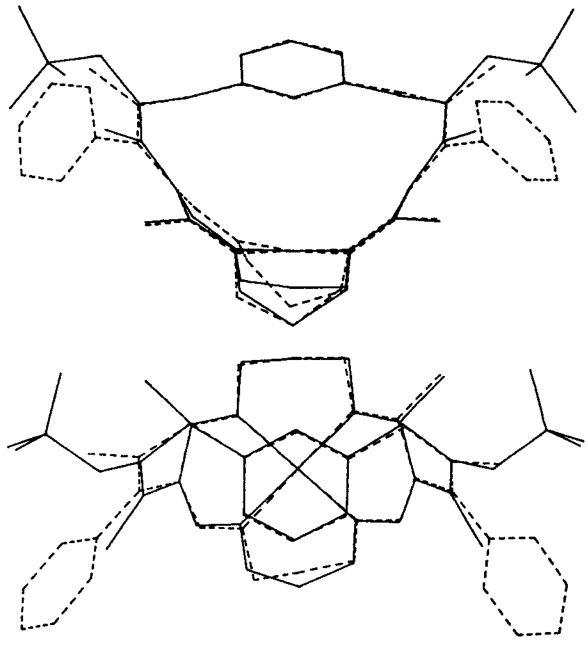

Figure 5 Skeletal comparison of **2a** and **2d**:(a) side view (b) top view.

Electrochemical data were obtained using a Princeton Applied Research Corp. potentiostat/galvanostat Model 173 equipped with a Model 175 linear programmer and a Model 179 digital coulometer. Cyclic voltammograms were measured in acetonitrile at the platinum disk working electrode in 0.1 M TBAT electrolyte with potentials measured versus a $Ag/AgNO_3/CH_3CN$ reference electrode. Half-wave potentials were taken as the average of the anodic and cathodic peak potentials at a scan rate of 100 mv/sec.

Visible and ultraviolet spectra were obtained using a Varian model 2300 recording spectrophotometer. Samples were prepared as solutions in 1 cm quartz cells. Oxygen titrations were performed using a series of computer-interfaced rotameters to control gas flow. During titration, samples were temperature controlled to ± 0.1°C using a Neslab constant-temperature circulation system.

Synthesis of Unbridged Nickel Complexes.—**[2,12-dimethyl-3,11-bis(1-methoxyethylidene)-1,5,9,13-tetraazacy clohexadeca-1,4,9,12-tetraene-^{4}N]nickel (II) Hexafluorophosphate, Ni{EtOEthi)$_2$Me$_2$[16]-tetraeneN$_4$}](PF$_6$)$_2$**. This complex was synthesized using the procedure of Schammel.[8,13]

(1a)(2,12-Dimethyl-3,11-bis[1-(1-dimethyl-2-dimethylamino-ethylamine)-ethylidene]-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraeneK^{4}N$_4$)nickel(II) Hexafluorophosphate. As 1-dimethylamino-2-amino-2-methylpropane (2.09 g, 20.5 mmol) was added dropwise to a stirred solution of [Ni{(EtOEthi)$_2$Me$_2$[16]-tetraeneN$_4$}](PF$_6$)$_2$ (6.05 g, 8.2 mmol) in acetonitrile (125 mL) an immediate color change from green to red occurred. After stirring for 5 hours the solution was evaporated to dryness *in vacuo*. The gold solid was collected and purified by chromatography using neutral alumina using acetonitrile:methanol (98:2) as the eluant. The rapidly moving yellow band was collected, reduced to a low volume *in vacuo* and methanol was added to effect precipitation. The gold solid (4.6 g, 5.3 mmol, 64%) was characterized by ^{13}C NMR.

(1b)(2,12-Dimethyl-3,11-bis[1-diphenylmethylamine)ethylidene]-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraeneK^{4}N$_4$)nickel(II) Hexafluorophosphate. This was prepared similarly using diphenylamine. The gold-colored solid was characterized by ^{13}C NMR.

(1c)(2,12-Dimethyl-3,11-bis[1-(neo-pentylamine)ethylidene]-1,5,9,1 3-tetraaza-cyclohexadeca-1,4,9,12-tetraeneK^{4}N$_4$)nickel(II) Hexafluoro-phosphate. A red solution immediately formed as neo-pentylamine (0.77 g, 8.46 mmol) was added slowly to a stirring solution of [Ni{(MeOEthi)$_2$Me$_2$[16]tetraene N$_4$}](PF$_6$)$_2$ (3.0 g, 4.2 mmol) in 100 mL of acetonitrile. Under reduced pressure the volume was reduced to 15 mL at which time methanol (50 mL) was added. After 3 days at 0 °C, a yellow solid was collected (2.47 g, 3.0 mmol, 71%).

(1d) [2,12-Dimethyl-3,11-bis(1-(2,2-diphenylethylamino)ethylidene)-1, 5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-^{4}N)nickel(II) Hexafluorophosphate. 2,2′-Diphenyl ethylamine (1.2 g, 6.1 mmol) was added to a stirred solution of {Ni{(MeOEthi)$_2$Me$_2$[16]tetraene N$_4$}](PF$_6$)$_2$ (2.0 g, 2.82 mmol) in 120 mL acetone. After thirty minutes, the color changed from an initial deep red to amber. The solvent was gradually removed on a rotary evaporator while methanol was occasionally added to promote precipitation of the product. The yellow powdery precipitate was collected by filtration and dried *in vacuo*. Yield: 89%.

Synthesis of Bridged Ni(II) Cyclidene Complexes.—Attempts to prepare bridged complexes from **1a** and **1b**, using either α,α′-dibromo-m-xylylene (**1a**) or 1,6-ditosylhexane (**1b**) using similar procedures to those described next were unsuccessful, with no bridged complexes being recoverable.

(2a) [3,11-Bis(neo-pentyl)-14,20-dimethyl-3,11,15, 19,22,26-hexaazatricyclo-[11.7.7^{1,13}.1^{5,9}]octacosa-1,5,7,9(28),12,14,19,21,26-nonaene-K^{4}N-nickel(II)] Hexafluorophosphate. When yellow solid [Ni{Me$_2$ (neo-pentyl)$_2$H$_2$[16]cyclidene}](PF$_6$)$_2$(**1c**) (2.47 g, 3.0 mmol) was added to a stirring solution of $NaOCH_3$ (0.35 g, 6.3 mmol) in degassed acetonitrile (500 mL) under a blanket of a nitrogen gas, the solution displayed a red color. After heating to reflux, α,α^1-dibromo-m-xylylene (0.8 g, 3.30 mmol) dissolved in acetonitrile (120 mL) was added via a peristaltic pump over a 2 hr period. The reaction mixture was heated at reflux for 8 hr, cooled to room temperature, and the solvent was reduced to a low volume *in vacuo*. This solution was filtered through Celite 545, collected and concentrated to an oil. The oil was dissolved in a minimum amount of acetonitrile and purified by chromatography through a neutral alumina column with acetonitrile as the elutant. The first fraction, a yellow band, was collected and evaporated to dryness *in vacuo*, producing a yellow solid which was recrystallized from an acetonitrile/methanol mixture. Deep yellow blocks of a chloroform solvate suitable for x-ray analysis were obtained from chloroform (1.02 g, 1.1 mmol, 37%). Anal. Calcd. for $NiC_{36}H_{56}N_6P_2F_{12}°$ 1.7$HCCl_3$: C, 40.26; H, 5.17; N, 7.47; Cl, 16.07. Found: C, 40.27; H, 5.16; N, 7.22; Cl, 16.92. FAB mass spectrum parent peak 631a as expected for $[C_{36}H_{56}N_6Ni]^+$.

(2b) [2,12,13,20-tetramethyl-3-11-(2,2-diphenylethyl)-3,11,15,19,22,26-hexaazatricyclo [11°7°7°1^{5,9}]octacosa 1,5,7,9(28),12,14,19,21,26 nonaene-^{4}N]nickel(II) Hexafluorophosphate. This complex was prepared following the published procedure,[8] using **1d** (1.8 g, 1.73 mmol) in 150 mL acetonitrile and α,α′-dibromo-m-xylylene (0.47 g, 1.78 mmol) in 160 mL acetonitrile. Following chromatography on a 3 x 25 cm neutral alumina column, the mobile yellow band was collected and then evaporated with the slow addition of a methanol to give a yellow precipitate. Yield: 1.1 g, 56%.

Anal: Calc. for $C_{45}H_{60}N_6P_2F_{12}Ni$: C, 56.81; H, 5.30; N, 7.36. Found: C, 56.25; H, 5.52; N, 7.09.

(2c) [2,11,13,19-tetramethyl-3,10-(2,2-diphenylethyl)-3,10,14,18,21,2 5-hexaazabicyclo[10·7·7]hexacosa 1,11,13,18,20,25-hexaene-^{4}N]nickel(II) Hexafluorophosphate. This was prepared by the method of Stevens and Busch[1b,8] using **1d** (1.02 g, 0.98 mmol) in 108 mL of acetonitrile and 1,6-bis(p-toluenesulphonato)hexane(0.469, 1.09 mmol) in 110 mL of acetonitrile. Following chromatography on neutral alumina using acetonitrile as eluent, the first half of the mobile yellow band was collected, methanol was added, and solvent was slowly removed (25-30 °C) on a rotary evaporator, with additional methanol added as necessary to promote precipitation of the product, which can be recrystallized using methanol and acetonitrile at reduced temperature. Yield: 40%. Anal: Calc. for $C_{52}H_{64}N_6P_2F_{12}$ Ni: C, 55.68; H, 5.75; N, 7.49. Found: C, 55.53; H, 5.92; N, 7.69.

Ligand Salts.—

(3a) [2,12,13,20-tetramethyl-3,11-(2,2-diphenylmethyl) 3,11,15,19,22,26-hexaazatricyclo[11.7.7.1^{5,9}] octacosa-1,5,7,9(20,12,14,19,21,26(nonaene-^{4}] Hexafluorophosphate. This demetallated ligand salt was prepared by bubbling a vigorous stream of dry HBr gas through a slurry of 0.75 grams (0.66 mmol) of the insoluble **2b** (0.7 b, 0.66 mmol) in 100 mL of dry methanol. The gas was bubbled fast enough to sustain a hanging white smoke above the solution in the flask. While bubbling, the solution changed from a light greenish-yellow to a darker red, to an emerald green that persisted only while a strong flow of HBr was maintained. After 45 min, the solvent in the now-warm flask was removed by rotary evaporation, leaving a gummy green residue. This was redissolved in 10 mL of water and enough additional methanol to complete dissolution. The flask was chilled in ice, and a solution of ten equivalents of ammonium hexafluorophosphate in 20 mL of water was slowly (10 min) dripped in, precipitating the project as a gummy solid, which was filtered and washed with water (to dissolve the excess NH_4PF_6). Several days *in vacuo* were required to dry the hydroscopic yellow solid. Drying was facilitated by frequently spreading the gummy material on the side of the drying container and repeating the spreading after more drying had taken place. Yield: 0.74 g, 94%.

(3b)[2,11,13,19-tetramethyl-3,10-(2,2-diphenylethyl) 3,10,14,18,21,25-hexaazabicyclo [10.7.7]hexacosa 1, 11,13,18,20,25-hexaene-k^{4}N] Hexafluorophosphate. This was prepared by the same method as **3a**, to give an off-white product. Yield: 93%.

Synthesis of Cobalt(II) Bridged Complexes.—

(4a)[2,12,13,20-tetramethyl-3,11-(2,2-diphenylethyl)-3,11,15,19, 22,26-hexaazatricyclo[11. 7.7.1^{5,9}]octacosa-1,5,7,9(28),12,14,19, 21,26-nonaene-k^{4}N]cobalt(II) Hexafluorophosphate. In an oxygen-free glove box, **3a** (0.73 g, 0.593 mmol) was slurried in 15 mL of hot methanol on a hot plate. To this was added a purple solution of 0.149 g (0.594 mmol) of cobalt(II) acetate tetrahydrate (0.089 g, 0.59 mmol) and 0.082 g (0.593 mmol) of sodium acetate trihydrate (0.089 g, 0.59 mmol) in 10 mL of hot methanol. Upon addition, the solution immediately turned orange, and an orange microcrystalline product began to precipitate. The solution was cooled and the product collected by suction filtration. Yield: 0.56 g, 82%.

(4b) [2,11,13,19-tetramethyl-3,10-(2,2-diphenyl-ethyl) 3,10,14,18, 21,25-hexaazabicyclo[10.7.7]hexacosa 1,11,13,18,20,25-hexaene-k^{4}N]cobalt(II) Hexa-fluorophosphate. This compound was prepared by the same method as 4a. Yield: 82%.

Crystal Structure Analysis.—Crystal data: **2a**: $NiC_{36}H_{56}N_6P_2F_{12}.2CHCl_3$, M = 921.5+238.7, Monoclinic, $P2_1/c$, a = 13.463(1), b = 14.506(2), c = 26.724(2)Å, β = 91.45°, V = 5217(1) Å^3, Z = 4, D_c 1.48 g cm^{-3}, D_m = 1.46 g cm^{-3} (flotation), graphite-monochromatised M$_o$-K$_a$ radiation, λ = 0.71069A, (M $_o$-K$_a$) = 5.55 cm^{-1}, T = 293K. 2d: : $NiC_{33}H_{40}N_6P_2F_{12}.C_2H_6O$,M = 869.3+46.1, Monoclinic, $P2_1/c$, a = 24.721(6), b = 10.934(3), c = 16.321(5)Å, β = 97.30(2)°, V = 4376(2) Å^3, Z = 4, D_c 1.39 g cm^{-3}, graphite-monochromatised M$_o$-K$_a$ radiation, λ = 0.71069A, (M $_o$-K$_a$) = 6.02 cm^{-1}, T = 293K.

Collection and Refinement.—(Information for **2d** is given in parentheses.) Data were collected with a Syntex $P2_1$ diffractometer in θ-2θ mode. Maximum θ was 45° with scan range 0.9° (θ) about the Kα1 – Kα2 positions; scan speed 4(2) -29 deg min^{-1}. Backgrounds were measured at each end of the scan for 0.5 (0.25) of the scan time. Three standard reflections were monitored every 50 (200) reflections and showed slight fluctuations during data collection, corrected by a moving rescale procedure. Unit cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections (20<2θ<22 deg). 5853 (5749) unique reflections (r_{int} = 0.026 (0.022)); 3895 (2992) were considered observed (I/σ(I)> = 2.0(3.0)) and were corrected for Lorentz, and polarization. For **2d**, a correction was also made for absorption effects, by the analytical method with maximum and minimum transmission factors of 0.93 and 0.81. Crystal sizes: 0.38 x 0.39 x 0.30 (0.15 x 0.52 x 0.35) mm.

Systematic reflection conditions h01,1=2n; 0k0, k=2n identify both space groups as $P2_1/c$. Both structures were solved by locating the nickel atom from a Patterson map, and the remaining non-hydrogen atoms were then found on successive Fourier syntheses. For **2a**, two chloroform solvent molecules were found; both Cl and F atoms had high thermal parameters, but showed no signs of multiple occupancies, though the highly anisotropic thermal motion of C(6) suggests partial chair-boat disorder. For **2d**, a solvent ethanol molecule was located (given 0.5 occupancy, refined isotropically). Anisotropic tempera-

Table 5a Atom coordinates (x10^4) and isotropic thermal parameters (A^{2}x10^3) for **2a**

Atom	*x*	*y*	*z*	*U*
	1070.6(9)	1186.3(8)	4119.7(5)	47(1)*
(1)	-133.6(27)	7671.4(23)	3990.3(13)	75(1)*
(2)	5555(3)	1794(3)	4071(2)	87(2)*
(11)	-997(7)	6994(7)	3910(5)	181(6)*
(12)	719(7)	8359(7)	4060(4)	167(5)*
(13)	-802(6)	8257(6)	4342(3)	126(4)*
(14)	-519(7)	8237(6)	3533(3)	141(4)*
(15)	270(7)	7111(5)	4450(3)	124(4)*
(16)	492(7)	7022(6)	3648(3)	143(4)*
(21)	4618(8)	1291(9)	3897(6)	244(8)*
(22)	5477(11)	2319(14)	3592(6)	261(10)*
(23)	6492(7)	2313(7)	4225(5)	193(6)*
(24)	5700(12)	1146(13)	4479(7)	296(11)*
(25)	4918(12)	2461(13)	4274(8)	319(12)*
(26)	6211(11)	1142(13)	3811(9)	294(12)*
(001)	2774(12)	6703(12)	2331(6)	126(5)
L(11)	1632(6)	7162(5)	2474(3)	252(5)*
L(12)	2758(7)	5525(3)	2390(2)	255(5)*
L(13)	3682(5)	7185(4)	2722(2)	196(3)*
(002)	4030(9)	3991(9)	1394(5)	93(4)
L(21)	4453(4)	3589(4)	2002(2)	197(3)*
L(22)	4757(3)	3432(5)	947(3)	209(4)*
L(23)	2824(2)	3616(3)	1324(2)	111(2)*
(1)	2047(6)	373(5)	3880(3)	51(3)*
(2)	159(6)	629(6)	3670(4)	68(4)*
(3)	99(6)	1988(6)	4351(3)	57(3)*
(4)	1979(6)	1785(5)	4556(3)	48(3)*
(5)	2417(6)	777(5)	2354(3)	52(3)*
(6)	2196(6)	4560(5)	4128(3)	49(3)*
(1)	2147(8)	147(6)	3414(5)	54(4)*
(2)	2931(9)	-537(8)	3260(5)	77(5)*
(3)	1408(8)	407(6)	3046(4)	54(4)*
(4)	409(8)	430(7)	3222(5)	65(5)*
(5)	-889(9)	479(10)	3802(6)	110(7)*
(6)	-1282(10)	1064(13)	4107(7)	160(10)*
(7)	-917(8)	1687(8)	4463(5)	71(5)*
(8)	278(8)	2850(8)	4404(4)	60(4)*
(9)	1243(7)	3259(6)	4400(3)	41(3)*
(10)	2018(7)	2675(7)	4604(3)	50(4)*
(11)	2778(8)	3091(8)	4976(4)	70(5)*
(12)	2666(8)	1199(7)	4873(4)	66(4)*
(13)	2443(9)	194(7)	4782(4)	72(5)*
(14)	2688(9)	-96(7)	4257(5)	70(5)*
(15)	1560(8)	491(7)	2529(4)	57(4)*
(16)	730(9)	291(9)	2145(5)	92(6)*
(17)	2662(8)	822(7)	1812(4)	64(4)*
(18)	3298(11)	23(9)	1623(5)	87(6)*
(19)	2754(12)	-886(9)	1659(6)	123(8)*
(20)	3476(11)	274(10)	1082(5)	104(6)*
(21)	4276(10)	-36(11)	1913(5)	111(7)*
(22)	3075(7)	1360(6)	2666(4)	56(4)*
(23)	2580(7)	2247(6)	2831(4)	44(4)*
(24)	2901(7)	2665(6)	3264(4)	43(4)*
C(25)	2495(7)	3498(6)	3419(3)	45(4)*
C(26)	1738(9)	3885(7)	3123(4)	70(5)*
C(27)	1413(9)	3469(7)	2698(4)	72(5)*
C(28)	1827(9)	2643(7)	2544(4)	67(5)*
C(29)	2923(7)	3968(6)	3872(4)	53(4)*
C(30)	2374(8)	5568(7)	4061(4)	60(4)*
C(31)	2939(8)	6047(7)	4492(4)	65(4)*
C(32)	3058(10)	7050(7)	4317(6)	94(6)*
C(33)	3956(8)	5622(9)	4592(6)	92(6)*
C(34)	2345(9)	6018(7)	4970(4)	74(5)*
C(35)	1345(7)	4204(7)	4285(3)	47(4)*
C(36)	436(8)	4827(7)	4307(5)	68(5)*

Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Table 5b Atomic coordinates (x10^4) and isotropic thermal parameters (Å^{2}x10^3) for 2d.

	x	*y*	*z*	*U*
Ni	2432(1)	5601(1)	5778(1)	35(1)*
P(1)	9173(1)	3570(2)	6500(2)	59(1)*
P(2)	6106(1)	816(3)	4327(2)	67(1)*
F(11)	8779(4)	3869(7)	7141(6)	159(5)*
F(12)	9659(4)	4018(7)	7113(6)	142(4)*
F(13)	9590(4)	3216(9)	5884(5)	147(5)*
F(14)	8705(4)	3148(8)	5838(7)	178(5)*
F(15)	9246(4)	2227(6)	6834(5)	131(4)*
F(16)	9093(4)	4891(6)	6177(5)	139(4)*
F(21)	6324(4)	-508(7)	4573(6)	140(5)*
F(22)	5536(4)	429(10)	4454(9)	219(7)*
F(23)	6019(7)	379(11)	3449(6)	247(9)*
F(24)	5880(4)	2102(7)	4075(6)	170(5)*
F(25)	6192(5)	1157(10)	5235(5)	186(6)*
F(26)	6675(4)	1193(10)	4177(9)	211(7)*
C(01)	2312(12)	9061(22)	4202(16)	87(8)
C(02)	2246(11)	10459(23)	4669(15)	94(8)
O(01)	1977(12)	9053(24)	3661(18)	182(11)
N(1)	1761(3)	5843(5)	6161(4)	44(3)*
N(2)	2092(3)	4568(6)	4928(4)	41(3)*
N(3)	3102(3)	5432(7)	5361(4)	49(3)*
N(4)	2805(4)	6419(6)	6710(4)	41(3)*
N(5)	1076(3)	2478(6)	6726(5)	47(3)*
N(6)	3945(3)	3983(6)	7925(5)	56(3)*
C(1)	1386(4)	4987(7)	6182(5)	41(3)*
C(2)	856(4)	5280(8)	6505(7)	59(4)*
C(3)	1431(4)	3837(7)	5768(5)	32(3)*
C(4)	1725(4)	3823(7)	5090(5)	42(4)*
C(5)	2309(5)	4440(10)	4147(6)	70(5)*
C(6)	2650(5)	5486(11)	3955(6)	79(5)*
C(7)	3160(4)	5607(11)	4492(5)	64(4)*
C(8)	3528(4)	5113(8)	5852(6)	49(4)*
C(9)	3570(4)	5114(8)	6717(5)	45(4)*
C(10)	3253(4)	6042(8)	7087(5)	38(4)*
C(11)	3539(5)	6732(9)	7818(6)	67(5)*
C(12)	2555(4)	7565(7)	6975(6)	60(4)*
C(13)	2079(4)	7939(8)	6410(6)	55(4)*
C(14)	1603(4)	7095(7)	6379(6)	50(4)*
C(15)	1129(4)	2787(7)	5951(5)	40(4)*
C(16)	879(4)	2008(8)	5270(6)	54(4)*
C(17)	542(4)	2515(9)	4635(5)	50(4)*
C(18)	301(4)	1775(11)	3990(6)	73(5)*
C(19)	421(5)	549(10)	3977(7)	86(5)*
C(20)	740(7)	45(11)	4602(8)	129(8)*
C(21)	965(6)	746(9)	5257(8)	108(6)*
C(22)	653(5)	1643(10)	6945(7)	73(5)*
C(23)	1479(4)	2922(9)	7421(5)	49(4)*
C(24)	2063(4)	2643(8)	7357(5)	42(4)*
C(25)	2219(5)	1580(8)	6956(6)	57(4)*
C(26)	2745(5)	1315(9)	6971(6)	58(4)*
C(27)	3155(4)	2032(9)	7369(6)	58(4)*
C(28)	3009(4)	3119(8)	7768(5)	51(4)*
C(29)	2462(4)	3405(8)	7729(5)	42(4)*
C(30)	3440(4)	3892(10)	8270(6)	61(4)*
C(31)	4422(7)	3552(19)	8473(10)	84(7)*
C(32)	3985(4)	4405(8)	7149(6)	53(4)*
C(33)	4464(4)	4041(8)	6757(6)	53(4)*
C(34)	4838(5)	4925(10)	6563(7)	82(5)*
C(35)	5249(6)	4615(12)	6106(10)	116(7)*
C(36)	5329(5)	3440(10)	5899(8)	91(6)*
C(37)	4990(5)	2582(10)	6081(8)	92(6)*
C(38)	4567(5)	2851(9)	6521(7)	79(5)*

*Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor ture factors were used for all non H-atoms, unless noted. Hydrogen atoms were given fixed isotropic temperature factors (U = 0.08 (0.07)Å^2) and inserted at calculated positions without refinement; methyl groups were treated as rigid CH_3 units and solvent protons were omitted. Final refinement was on F by cascaded least-squares methods, refining 603 (556) parameters. Largest residual peaks were of height +0.7, -0.5 (+0.7, -.05).el.Å^{-3}. A weighting scheme of the form $W = 1/(\sigma(F)^2 + gF^2)$ with g = 0.00096 (0.0030) was used and shown to be satisfactory by a weight analysis. For **2a**, final R = 0.082, R_w = 0.093 (0.074, 0.078); such relatively high values are often found with this class of compounds, and are not unexpected for weakly-scattering crystals containing solvent and ions with high thermal motion. S(goodness-of-fit) = 1.78 (1.50). Final computing was with SHELXTL PLUS[14] (SHELXTL[15]) and scattering factors in the analytical form and anomalous dispersion factors were taken from reference 16. Final atomic coordinates are listed in **Table 5**.

Supplementary data available: Full bond lengths and angles, H-atom coordinates, anisotropic thermal parameters for **2a** and **2d**.

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