

S0277-5387(96)00206-9

Divalent metal chloride amidine complexes—2. Compounds of Mn, Co and Ni

Deirdre I. Arnold, F. Albert Cotton,* David J. Maloney and John H. Matonic

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, TX 77843, U.S.A.

and

Carlos A. Murillo*

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, TX 77843, U.S.A. and Department of Chemistry, University of Costa Rica, Ciudad Universitaria, Costa Rica

(Received 12 March 1996; accepted 23 April 1996)

Abstract—A series of compounds of the type $[MCl_2(amidine)_2]_n$, M = Mn, Co and Ni, has been prepared in high purity and yield by solubilizing otherwise insoluble metal chlorides in the presence of neutral amidines in refluxing toluene. As crystalline solids, they are stable in air for several days. The compounds are excellent starting materials for the formation of dinuclear compounds. A complete chemical and structural characterization is provided for the penta-coordinated dimanganese compound $[MnCl_2(HDPhF)_2]_2$, I (DPhF = diphenylformamidinato), the mononuclear compounds $CoCl_2(HDPhBz)_2$, II (DPhBz = diphenylbenzamidinato), and NiCl_2(HDTolF)_2, III (DTolF = di-*p*-tolylformamidinato). The HDPhF analogue of III reacts with a strong base to give the dinuclear species Ni₂(DPhF)₄ (IV), the structure of which is also reported here. Copyright © 1996 Elsevier Science Ltd

The use of amidinato ligands of the type $RNC(R')NR^-$ has met with considerable success for the preparation of transition metal complexes, especially of the dinuclear type.¹ In part 1² of this two-part report, the synthesis and structural characterization of a series of divalent metal chloride formamidines, $M^{II} = Fe$, Co and Pt was described.

At the time, we indicated that "the facility with which they form and the high purity in which they are isolated, as well as their favourable solubility characteristics, make them attractive starting materials for the preparation of other formamidinato complexes". In this paper we will show that our predictions were correct and will present the synthesis and characterization of new MCl_2 (amidine)₂ compounds for M = Mn, Co and Ni as well as that of the dinuclear compound $Ni_2(DPhF)_4$.

EXPERIMENTAL

Materials and methods

All manipulations were performed under an atmosphere of nitrogen using standard Schlenk techniques. Samples for spectroscopic characterization were prepared in a Vacuum Atmospheres drybox under an atmosphere of argon. Toluene, THF and hexanes were purified by conventional methods and were freshly distilled from Na/K alloy under nitrogen immediately prior to use. MnCl₂, CoCl₂ and NiCl₂ were purchased from Aesar. Both

^{*} Author to whom correspondence should be addressed.

CoCl₂ and NiCl₂ were refluxed for 20 min with thionylchloride (obtained from Fisher Scientific), then dried under vacuum prior to use. Celite 545 (not acid washed) was purchased from Spectrum Chemical; *n*-butyllithium (1.6 M solution in hexanes) and HDPhF were purchased from Aldrich Chemical Co.; HDTolF was prepared according to a slight modification of a published procedure,³ HDPhBz was prepared by a literature method.⁴ Elemental analyses were provided by Canadian Microanalytical Service Ltd. IR spectra were obtained as Nujol mulls between CsI plates on a Perkin–Elmer 16PC FT-IR spectrophotometer and magnetic susceptibility measurements were made using in a Johnson–Matthey MSB-1 balance.

$[MnCl_2(HDPhF)_2]_2$ (I)

MnCl₂ (1.00 g, 7.94 mmol) was refluxed in THF for 2 h and the solvent was then eliminated under vacuum. To the activated solid was added HDPhF (3.01 g, 15.9 mmol). Warm toluene (50 cm^3) was then added to the mixture which was refluxed for 30 min while stirring. The yellowish solution was quickly filtered while hot and left undisturbed for 1 day in a Dewar flask. Many single crystals of the compound were collected by filtration and washed with hexanes $(2 \times 10 \text{ cm}^3)$. Yield: 3.00 g (76%). Found: C, 60.6; H, 4.8; N, 10.8. Calc. for C₅₂H₄₈Cl₄Mn₂N₈: C, 60.2; H, 4.7; N, 10.8%. IR (Nujol, cm^{-1}): 3340(s), 3185(m), 3109(m), 2723(w), 1639(s), 1601(s, sh), 1586(s), 1377(s), 1320(s), 1205(s), 1179(m), 1072(w), 1027(w), 975(w), 895(m), 753(s), 696(s), 630(s). The magnetic susceptibility corresponded to a magnetic moment of 5.88 BM per MnCl₂(HDPhF)₂ unit.

$CoCl_2(HDPhBz)_2$ (II)

 $CoCl_2$ (0.13 g, 1.0 mmol) and HDPhBz (0.50 g, 1.84 mmol) were stirred together in toluene (15 cm³) and heated overnight. The mixture was then filtered through Celite to remove excess CoCl₂. The filtrate was layered with hexanes (20 cm³) and allowed to stand at room temperature for 24 h, then placed in a freezer at -20° C for another 24 h. Crystals of the compound, some of which were suitable for X-ray diffraction, were collected by filtration and washed with hexanes $(2 \times 10 \text{ cm}^3)$. Yield: 0.48 g (70%). Found: C, 62.7; H, 5.2; N, 7.2. Calc. for $C_{38}H_{32}Cl_2CoN_4$: C, 62.2; H, 4.4; N, 7.6%. IR (Nujol, cm^{-1}): 3155(w), 3100(w), 2854(s), 1622(m), 1607(s), 1583(s), 1565(s), 1411(s), 1377(s), 1239(w), 1205(m), 1073(w), 1026(w), 830(m), 789(s), 772(s), 703(m). The magnetic susceptibility corresponded to a magnetic moment of 4.40 BM.

NiCl₂(HDTolF)₂ (III)

NiCl₂ (0.39 g, 3.0 mmol) and HDTolF (0.90 g, 4.0 mmol) were stirred together in toluene (20 cm^3) and warmed to 100°C as the colour changed from pale yellow to green. After about 1 h the mixture was dried in vacuo and hexanes (20 cm³) were added. The mixture was heated and quickly filtered to remove any unreacted ligand. The remaining dark green solid was redissolved in toluene (10 cm³) and filtered to remove the excess NiCl₂. The yield after drying was 0.70 g (61%). Crystals suitable for study by X-ray diffraction were obtained by dissolving 0.05 g of the green solid in toluene (5 cm³), layering with hexanes and cooling the solution to -20° C. Large green block-shaped crystals formed within 48 h. IR (Nujol, cm^{-1}): 3188(m), 3100(m), 1651(s), 1607(m), 1589(m), 1520(m), 1505(s), 1377(m), 1312(s, br), 1221(m), 1201(m), 1018(w), 989(m), 808(m), 753(w), 720(w), 571(w), 506(m), 496(w). The magnetic susceptibility corresponded to a magnetic moment of 3.54 BM.

$Ni_2(DPhF)_4$ (IV)

A solution of NiCl₂(HDPhF)₂ (0.10 g, 0.19 mmol), synthesized in the same manner as NiCl₂(HDTolF)₂, in toluene (15 cm³) was prepared and cooled to -78° C. NaEt₃BH (0.1 cm³, 0.10 mmol) was added to the stirring solution and the resultant dark green-brown mixture was stirred and kept at -78° C. After 1 h, *n*-butyllithium (0.24 cm³, 0.38 mmol) was slowly added and the mixture immediately changed to a deep brown colour. After the mixture had warmed to room temperature, it was filtered through Celite and the filtrate was layered with hexanes (20 cm³) and stored at -20° C. Within 2 days, dark brown crystals had formed at the bottom of the tube. The yield of this reaction was not optimized.

Structure determinations

Geometric and intensity data for I were collected at room temperature on a Rigaku AFC5R rotating Cu anode diffractometer, data for II, III and IV were gathered at -60° C on an Enraf–Nonius FAST area detector system, utilizing the software program MADNES.⁵ Detailed procedures have previously been described.⁶

Unit-cell refinement for I utilized 25 reflections in the range $35 \le 2\theta \le 50^{\circ}$ C. For II, III and IV indexing was performed on 50 reflections taken from three 10° ω -rotations in the range $0 \le \omega \le 100^{\circ}$ and unit-cell refinement used 250 reflections in the range $20 \le 2\theta \le 32^{\circ}$. In each case, the cell dimensions and Laue group were confirmed with axial images. All data were corrected for Lorentz and polarization effects. Three strong reflections measured periodically throughout the data collection for I showed no significant decay. An empirical absorption correction based on six ψ -scans was applied for I. Data were processed into SHELX format using the program TEXSAN⁷ and ABSURD⁸ for I, II, III and IV, respectively.

In all structures, the positions of heavy atoms were found in direct methods E-maps using the software solution program in SHELXTL.⁹ Subsequent cycles of least-squares refinement followed by difference-Fourier synthesis produced the positions of the remaining non-hydrogen atoms. For purposes of structure factor calculations, hydrogen atoms were placed in idealized positions. Details of data collection and refinement are given in Table 1. Selected bond distances and angles for I, II, III and IV are listed in Tables 2, 3, 4 and 5, respectively. Supplementary data for I, II, III and IV have been deposited with the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

[MnCl₂(HDPhF)₂]₂

The best way to prepare I is to start with finely divided $MnCl_2$ prepared by eliminating THF from $Mn(THF)_2Cl_2^{10}$ and then refluxing it with HDPhF in toluene. A brief refluxing time and the filtration of the hot reaction mixture are crucial steps to obtain good yields of the pure and homogeneous crystalline product.

The molecular structure of I is shown in Fig. 1. In the solid state the compound is composed of discrete dinuclear molecules. Each molecule possesses crystallographically imposed C_i symmetry. The manganese atoms are bound to five groups, namely two neutral HDPhF molecules, one terminal and two bridging chloride ions. A long metalmetal separation [3.798(2) Å] and a magnetic moment which corresponds to five unpaired electrons precludes the existence of any type of manganese–manganese bond. The dinuclear molecule is internally stabilized by the presence of short (3.11 Å) contacts between N(4) and Cl(2) due to an intramolecular hydrogen bond.

As seen in Table 2, the distribution of atoms about the manganese atom, as well as the bond distances, is very irregular. The Mn—N(3) bond, where N(3) is almost *trans* to Cl(1A), is 0.12 Å

longer than the Mn—N(1) bond. The bond asymmetry is also observed for the bridging chloride ions. The Mn—Cl(1) bond distance is ca 0.26 Å shorter than that of Mn(1A)—Cl(1). As it is frequently encountered in compounds which contain both terminal and bridging groups, the former bond is slightly shorter.

$CoCl_2(HDPhBz)_2$

In our earlier study² we prepared $CoCl_2$ (HDTolF)₂ by a melt reaction using CoCl₂ and HDTolF. We have found that such reactions sometimes yield a product that is slightly oily and, therefore, further purification steps are sometimes needed. If the reagents are refluxed in toluene the reaction preceeds more cleanly and in higher yields. We suggest the latter procedure as well as the use of an excess of $CoCl_2$ for the preparation of II. CoCl₂(HDPhBz)₂ displays the characteristic blue colour of tetrahedral Co^{II} compounds. Its reactivity is similar to that of its HDPhF analogue. The structure is illustrated in Fig. 2 and is very similar to the previously described CoCl₂(HDPhF)₂. The two chloride ions and a nitrogen atom of each HDPhBz group complete the pseudo-tetrahedral coordination sphere. As with all other known tetrahedral $MCl_2(amidine)_2$ compounds, there are N-N····Cl hydrogen bonds which help stabilize the molecules. In II, Cl(1) and N(4), and Cl(2)and N(2) have separations of 3.25 and 3.19 Å, respectively. Presumably the presence of hydrogen bonds contributes significantly to the observed chemical stability of the crystalline samples of $MCl_2(amidine)_2$, M = Mn, Fe, Co and Ni, as well as to the facility with which they are crystallized.

NiCl₂(HDTolF]₂ (III)

While the synthesis of this compound proceeds quite poorly as a melt reaction, it goes smoothly by refluxing in toluene, occurring in a fashion similar to the preparations of I and II. It is important to note, however, that the reflux reaction must be stopped after a relatively short time, otherwise a flocculent white solid precipitates from the reaction mixture. This solid renders the reaction mixture difficult to filter and its production dramatically lowers the yield of III. The white solid has not been characterized, but based on its colour and insolubility may be an oligometric or polymetric Ni^{II} octahedral species. It is also very important to use strictly anhydrous NiCl₂. The magnetic susceptibility of III (3.54 BM) falls within the range expected for tetrahedral Ni^{II} complexes.¹¹

The structure of III is shown in Fig. 3. The aver-

	Ι	Π	Ш	IV
Formula	$C_{52}H_{48}Cl_4Mn_2N_8$	C _w H _n ,Cl,CoN ₄	C"H"CI,N,Ni	C.,H.,N.,Ni,
Formula weight	1036.66	674.51	578.21	898.37
Space group	$P2_1/c$	$P\overline{1}$	$P2_1/c$	C2/c
a (Å)	13.106(1)	10.4516(6)	10.222(4)	13.841(4)
$p\left(\mathbf{\check{A}}\right)$	10.210(1)	17.292(2)	14.965(9)	13.665(9)
c (Å)	19.226(1)	10.384(3)	19.450(8)	22.792(8)
α (°)	06	105.33(1)	06	90 Ĵ
β (°)	108.362(6)	112.91(1)	100.23(3)	91.03(6)
γ(°)	06	88.15(1)	60	90
$V(\mathbf{A}^3)$	2441.7(3)	1661.9(5)	2928(2)	4310(3)
Ζ	2	0	4	, 4
$d_{ m calc}~({ m g~cm^{-3}})$	1.410	1.348	1.312	1.384
Crystal size (mm ³)	$0.35 \times 0.27 \times 0.25$	$0.35 \times 0.20 \times 0.20$	$0.20 \times 0.30 \times 0.40$	$0.30 \times 0.10 \times 0.10$
Absorption coefficient (mm^{-1})	6.573	0.710	0.870	0.921
Data collection instrument	Rigaku AFC5R	FAST	FAST	FAST
Radiation (monochromated in incident beam)	$\operatorname{Cu-}K_{\alpha}(\lambda_{\alpha}=1.54184 \text{ Å})$	$Mo-K_{\alpha}(\lambda_{\alpha}=0.71073 \text{ Å})$	$Mo-K_{x}(\lambda_{a} = 0.71073 \text{ Å})$	Mo- $K_{x}(\lambda_{x} = 0.71073 \text{ Å})$
Temperature (°C)	20(2)	-60(2)	-60(2)	-60(2)
Data collection range, θ (°)	3.55-60.11	2.21-22.5	2.44-22.50	2.27 - 21.00
Number of unique data, total with $F_{o}^{2} > 2\sigma(F_{o}^{2})$	3640	3728	3690	2021
Number of parameters refined	298	534	418	280
Transmission factors, min., max.	0.4865, 0.9995	ŀ		
R ^a	0.044	0.053	0.066	0.089
$\mathrm{w}R_2^b$	0.105	0.110	0.134	0.164
Quality-of-fit indicator	1.032	1.122	1.180	1.190

Table 1. Crystal data for [MnCl₃(HDPhF)₃], (I), CoCl₃(HDPhBz), (II), NiCl₃(HDTolF), (III) and Ni₅(DPhF), (IV)

 $^{\circ}WR_{2} = [2W(F_{0}^{\circ} - F_{0}^{\circ})^{2}/2W(F_{0}^{\circ})^{2}]^{1/2}$, $w = 1[\sigma^{2}(F_{0}^{\circ}) + (ap)^{2} + bp, p = \max(F_{0}^{\circ} \text{ or } 0) + 2(F_{0}^{\circ})]/3$. a = 0.0499 and b = 2.3830 for I, a = 0.0322, b = 4.657 for II; a = 0.0454 and b = 0.0556 for III; a = 0.0242 and b = 75.843 for IV.

1.298(5) 1.439(5) 1.350(6) 1.426(5) 1.297(5) 1.438(5) 1.349(6)
1.439(5) 1.350(6) 1.426(5) 1.297(5) 1.438(5) 1.349(6)
1.350(6) 1.426(5) 1.297(5) 1.438(5) 1.349(6)
1.426(5) 1.297(5) 1.438(5) 1.349(6)
1.297(5) 1.438(5) 1.349(6)
1.438(5) 1.349(6)
1.349(6)
1.431(6)
114.8(3)
125.5(3)
1) 119.6(3)
123.9(4)
114.6(4)
130.8(3)
1) 114.2(3)
125.6(4)
122.5(4)
120.0(4)

Table 2. Selected bond lengths (Å) and angles (°) for $[MnCl_2(HDPhF)_2]_2$ (I)"

"Atoms labelled with an "A" are related by an inversion centre.

Co(1)Cl(1)		2.270(2)	N(2) - C(1)	1.350(6)
Co(1)—Cl(2)		2.265(2)	N(2)—C(20)	1.419(6)
Co(1)—N(1)		2.033(4)	N(3)—C(2)	1.302(6)
Co(1)—N(3)		2.041(4)	N(3)—C(30)	1.438(6)
N(1) - C(1)		1.317(6)	N(4)—C(2)	1.356(6)
N(1)C(10)		1.450(6)	N(4)—C(40)	1.420(7)
Cl(1)—Co(1)—Cl(2	.)	111.06(6)	Co(1) - N(1) - C(1)	127.4(3)
Cl(1)-Co(1)-N(1))	108.5(1)	Co(1) - N(1) - C(10)	113.3(3)
Cl(1)-Co(1)-N(3))	109.6(1)	Co(1) - N(3) - C(2)	124.2(3)
Cl(2)—Co(1)—N(1))	111.3(1)	Co(1) - N(3) - C(30)	116.0(3)
Cl(2) - Co(1) - N(3))	103.5(1)	N(1) - C(1) - N(2)	117.9(5)
N(1)— $Co(1)$ — $N(3)$	1	112.8(2)	N(3) - C(2) - N(4)	117.2(4)

Table 3. Selected bond lengths (Å) and angles (°) for $CoCl_2(HDPhBz)_2$ (II)

Table 4. Selected bond lengths (Å) and angles (°) for NiCl₂(HDTolF)₂ (III)

Ni(1)Cl(1)	2.250(2)	N(2)—C(1)	1.322(7)
Ni(1)— $Cl(2)$	2.247(2)	N(2) - C(10)	1.426(7)
Ni(1) - N(1)	2.004(5)	N(3) - C(2)	1.310(7)
Ni(1)—N(3)	2.006(4)	N(4) - C(2)	1.331(7)
N(1) - C(1)	1.298(7)	N(4) - C(24)	1.412(7)
N(3)C(17)	1.436(7)		
Cl(1)NiCl(2)	120.33(8)	Ni-N(1)-C(1)	130.0(4)
Cl(1)—Ni—N(1)	105.2(1)	Ni - N(1) - C(3)	116.0(3)
Cl(1)—Ni—N(3)	106.3(1)	Ni - N(3) - C(2)	125.8(4)
Cl(2)NiN(1)	108.2(2)	Ni—N(3)—C(17)	119.5(3)
Cl(2)NiN(3)	115.5(1)	N(1) - C(1) - N(2)	123.3(6)
N(1)—Ni—N(3)	98.7(2)	N(3)—C(2)—N(4)	123.8(6)

Ni-Ni(A)	2.490(3)	N(1) - C(1)	1.31(1)
Ni-N(1)	1.922(9)	N(2)—C(2)	1.33(1)
NiN(2)	1.899(9)	N(3) - C(1A)	1.31(1)
NiN(3)	1.93(1)	N(4)—C(2A)	1.32(1)
NiN(4)	1.90(1)		
N(1)N(2)	174.5(4)	N(3)—Ni—N(4)	172.5(4)
N(1) - Ni - N(3)	89.4(4)	N(1) - C(1) - N(3A)	125(1)
N(1)— Ni — $N(4)$	89.4(4)	N(2) - C(2) - N(4A)	123(1)
N(2) - Ni - N(3)	89.9(4)	N(1)— Ni — $Ni(A)$ — $N(3A)$	14.5(4)
N(2)—Ni—N(4)	90.6(4)	N(2)— Ni — $Ni(A)$ — $N(4A)$	14.9(4)

Table 5. Selected bond lengths (Å) and angles (°) for $Ni_2(DPhF)_4$ (IV)^a

^a Atoms labelled with an "A" are related by a two-fold axis.

age Ni—Cl and Ni—N bond lengths are 2.249(2) and 2.005(1) Å, respectively. Short distances between the chloride ions and the protonated nitrogen atoms of the HDTolF molecules are a clear indication of the presence of hydrogen bonds. The Cl(1)—N(4) distance is 3.11 Å and the Cl(2)—N(2) separation is 3.20 Å.

In general, the trend of slightly shorter C-N (imido) as compared with C-N(amine) bond distances observed in other complexed and uncomplexed neutral amidines¹² is also seen here. Surprisingly, only a few tetrahedral Ni¹¹ species containing an N2Cl2 donor ligand set have been characterized by X-ray crystallography. When the nitrogen donor ligand is 3,4-dihydro-1-phenyl-lH-[1,4]oxazino[4,3-a]-benzimidazole, average Ni-Cl and

Ni—N distances are reported as 2.23(1) and 2.00(5) Å, respectively.¹³ The crystal structure of dichlorobis [2,4-bis(isopropylamino)-6-methoxy-1,3,5-triazene] nickel(II) has also been reported,¹⁴ in which the Ni¹¹ centre exists in a distorted tetrahedral environment and also has two long [2.700(7) Å] contacts with oxygen atoms of the ligands. Average Ni-Cl and Ni—N bond lengths for this compound are 2.281(2) and 2.017(8) Å, respectively.

$Ni_2(DPhF)_4(IV)$

The action of a strong base on the HDPhF analogue of III yields crystal of Ni₂(DPhF)₄, which is in all important respects identical with the previously reported Ni₂(DTolF)₄.¹⁵ Its molecular structure is



Fig. 1. Thermal ellipsoid plot of the dinuclear compound [MnCl₂(HDPhF)₂]₂. Atoms are represented by their 50% probability ellipsoids.

1 ľ



Fig. 2. Structural representation of $CoCl_2(HDPhBz)_2$. Atoms are represented by their 50% probability ellipsoids.

shown in Fig. 4. The long Ni—Ni separation [2.490(3) Å] is consistent with the absence of a bond. Four amidinato groups form bridges between the metal atoms, which have an essentially square planar coordination.

The main interest in the preparation of IV was to show that there exists a general pathway to the



Fig. 3. A plot of the molecular structure of $NiCl_2(HDTolF)_2$. Atoms are represented by their 50% probability ellipsoids.

synthesis of dinuclear amidinato compounds from species of the type $MCl_2(amidine)_2$. Table 6 contains a listing of several compounds of the types $M_2(amidinato)_3$ and $M_2(amidinato)_4$. Some of them have been made exclusively from mononuclear $MCl_2(amidine)_2$ compounds; those of the types $Fe_2(amidinato)_4$, $Fe_2(amidinato)_3$ and $Co_2(am$ $idinato)_3$ cannot be made using other classical synthetic pathways.

We have now been able to prepare various $MCl_2(amidine)_2$ compounds for M = Mn, Fe, Co, Ni and Pt. Except for the latter, our present results indicate that their preparation and purification is best accomplished if the reaction of the corresponding finely divided anhydrous metal dichloride and the amidine is carried out in a toluene solution. The fact that the stoichiometry is correct to produce the corresponding tetrabridged dimetal(II) species of elimination of 2 equiv. of HCl indicates that their use will probably produce a significant number of metal–metal bonded compounds, especially those of the post-chromium elements of the first transition series, which until now have been very difficult to synthesize.

Acknowledgements—We are grateful to the Vicerrectoría de Investigación U. C. R. (Project 115-87-516) and the Department of Chemistry for support of work at the Univeristy of Costa Rica and to the National Science Foundation for support of work at Texas A&M University. We also thank Dr L. M. Daniels for crystallographic advice.



Fig. 4. A drawing and labelling scheme of the molecular structure of Ni₂(DPhF)₄. Non-hydrogen atoms are shown as 50% probability ellipsoids.

Starting material	Dinuclear compound formed	Metal-metal separation (Å)	Reference
[MnCl ₂ (HDPhF) ₂] ₂		_	Work in progress
FeCl ₂ (HDPhF) ₂	$\begin{cases} Fe_2(DPhF)_3\\ Fe_2(DPhF)_4 \end{cases}$	2.2318(8) 2.462(2)	16 17
FeCl ₂ (HDPhBz) ₂	$Fe_2(\mu$ -DPhBz) ₂ (η^2 -DPhBz) ₂	3.124(1)	18
CoCl ₂ (HDPhF) ₂	$\begin{cases} Co_2(DPhF)_3\\ Co_2(DPhF)_4 \end{cases}$	2.385(1) 2.3735(9)	19 20
CoCl ₂ (HDPhBz) ₂	$\begin{cases} Co_2(DPhBz)_3\\ Co_2(DPhBz)_4 \end{cases}$	2.320(1) 2.298(2)	19 20
NiCl ₂ (HDPhF) ₂	Ni ₂ (DPhF) ₄	2.490(3)	This work
trans-PtCl ₂ (HDPhF) ₂	$\begin{cases} Pt_2(\mu\text{-}DPhF)_2(\eta^2\text{-}DPhF)_2\\ Pt_2(\mu\text{-}DPhF)_4 \end{cases}$	2.9128(9) 2.649(2)	21 21

Table 6. Some dinuclear compounds prepared from MCl₂(amidine)₂ starting materials

REFERENCES

- See for example, F. A. Cotton, L. M. Daniels and C. A. Murillo, *Inorg. Chem.* 1993, 32, 2881, and refs therein.
- F. A. Cotton, L. M. Daniels, D. J. Maloney, J. H. Matonic and C. A. Murillo, *Polyhedron* 1994, 13, 815.
- 3. R. M. Roberts, J. Org. Chem. 1949, 14, 277.
- 4. A. C. Houtz and E. C. Wagner, *Organic Synthesis*, Collective Vol. 4, p. 383. John Wiley & Sons, New York.
- 5. J. Pflugrath, A. Messerschmitt MADNES, Munich

Area Detector (New EEC) System, Version EEC 11/1/89, with enhancements by Enraf-Nonius Corporation, Delft, The Netherlands. A description of MADNES appears in: A. Messerschmitt and J. Pflugrath, J. Appl. Cryst. 1987, 20, 30.

- (a) J. C. Bryan, F. A. Cotton, L. M. Daniels, S. C. Haefner and A. P. Sattelberger, *Inorg. Chem.* 1995, 34, 1875;
 (b) W. R. Scheidt and I. Turowska-Turk, *Inorg. Chem.* 1994, 33, 1314.
- 7. TEXSAN-TEXRAY. Structure Analysis Package. Molecular Structure Corporation (1985).
- 8. P. R. Evans, ABSURD. Absorption Correction Program for the Area Detector. MRC Laboratory of

Molecular Biology, Hills Road, Cambridge, U.K. (1990).

- 9. SHELXTL, Version 5.03. Siemens Industrial Automation Inc, Madison, Wisconsin, U.S.A.
- A. Hosseiny, C. A. McAuliffe, K. Minten, M. J. Parrott, R. Pritchard and J. Tames, *Inorg. Chim. Acta* 1980, **39**, 227.
- L. Sacconi, F. Mani and A. Bencini, *Comprehensive Coordination Chemistry* (Edited by G. Wilkinson, R. D. Gillard and J. A. McCleverty), Vol. 4, Ch. 50, p. 54. Pergamon Press, Oxford, U.K. (1987).
- 12. F. A. Cotton, S. C. Haefner, J. H. Matonic, C. A. Murillo and X. Wang, *Polyhedron*, in press.
- B. Piggott and A. C. Skapsi, *Inorg. Chim. Acta* 1983, 77, L171.
- 14. G. Reck, A. Kircheiss, R. Bauwe and H. Schrauber, Cryst. Struct. Commun. 1982, 11, 1147.

- F. A. Cotton, M. Matusz, R. Poli and X. Feng, J. Am. Chem. Soc. 1988, 110, 1144.
- F. A. Cotton, L. M. Daniels, L. R. Falvello and C. A. Murillo, *Inorg. Chim. Acta* 1994, **219**, 7.
- 17. F. A. Cotton, L. M. Daniels and C. A. Murillo, *Inorg. Chim. Acta* 1994, 224, 5.
- 18. F. A. Cotton, J. H. Matonic and C. A. Murillo, unpublished results.
- F. A. Cotton, L. M. Daniels, D. J. Maloney and C. A. Murillo, *Inorg. Chim. Acta* 1996, **249**, 9.
- F. A. Cotton, L. M. Daniels, X. Feng, D. J. Maloney, J. H. Matonic and C. A. Murillo, *Inorg. Chim. Acta*, accepted.
- 21. F. A. Cotton, J. H. Matonic and C. A. Murillo, *Inorg. Chem.* 1996, **35**, 498.