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Octahedro octahedra and tetrahedra
II. Tetra- to heptanuclear carbonyl(cyano)chromato, -molybdato and -tungstato complexes of 3d metals

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Abstract

A series of mostly homoleptic supercomplexes has been synthesized and characterized in which a central metalloid (Si^{IV}, Ge^{IV}, Sn^{IV}) or (3d) metal (Cr^{III}, Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{I}, Zn^{II}) is surrounded by up to six 'ligand complexes' $[NCM'(CO)_5]^-$ ($M' = Cr^0$, Mo^0, W^0). X-ray structures are reported for the heptanuclear six-coordinate $(NEt_4)_2[Si\{NCCr(CO)_5\}_6]$ (**1a**) ('octahedro octahedron'), the hexanuclear five-coordinate $(NEt_4)_3[Ni\{NCW(CO)_5\}_5]$ (**8c**) and the (heteroleptic) tetranuclear four-coordinate $(NEt_4)_2[Co(Cl)\{NCCr(CO)_5\}_3]$ (**7d**), the most striking feature being the co-existence in all complex anions of linear and distinctly bent $M'-C\equiv N-M$ linkages. An approximately square-pyramidal coordination sphere is established for the nickel ion in **8c**. Generally, the peripheral atoms and groups (oxygen, methyl) are found in rather ill-defined positions due to their high thermal motion. In the spectrochemical series, a position slightly above *N*CS$^-$ (i.e. towards the stronger end) is deduced for the $[NCM'(CO)_5]^-$ ($=A$) ligands from Vis–UV spectra. Negative FAB mass spectra reveal the presence in the matrix of the cluster anions $[MA_3]^-$, $[MA_4, NEt_4]^-$ ($[CuA_2]^-$, $[CuA_3, Cu]^-$). Thermolysis of **7a** and **10a** proceeds in two steps with loss of, initially, $Cr(CO)_6$ followed by CO and HCN as established by mass chromatography.

Introduction

As prevalent as the cyanide ligand was in early coordination chemistry [1, 2], its use in modern organometallic and cluster chemistry has been correspondingly rare. Recently, however, a kind of renaissance of the CO-like species CN^- and CNH is observed covering the whole range from metal-promoted and -catalyzed organic syntheses to polymeric materials with specifically designed properties [3–9]. On the other hand, there has been continuous interest throughout the years in cyanide-bridged homo- and heterodinuclear metal complexes particularly in connection with studies of reaction kinetics [10], charge-transfer processes [11] and electrochemical transformations [12, 13].

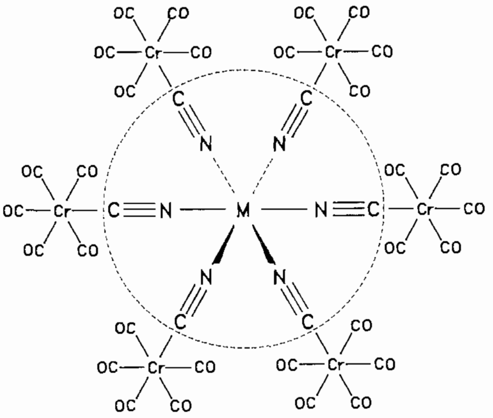

Fig. 1. Schematic drawing of the heptanuclear hexaisocyano ('oo') complexes **1a**–**4a**.

Prior to our preliminary report on 'cyano complexes as ligands' which dealt with sixfold pentacarbonylchromium-stabilized hexaisocyano complexes of silicon, germanium and tin (Fig. 1) [14], there was only the paper by Edelmann and Behrens on a similar tetranuclear Cr^{III}/Cr^0 species [15] apart from Siebert's classical work on oligonuclear adducts between $[Co(CN)(NH_3)_5]^{2+}$ and Ag^+ or Hg^{2+} (already termed 'supercomplexes' (!)) [16], and some cyclic organometallic tetramers ($[AuPr^n{}_2CN]_4$, $[\{Pd(\eta^3\text{-}C_3H_2Me_3\text{-}1,2,3)(CN)\}_4]$) [17]. Meanwhile, numerous articles have appeared on oligonuclear non-polymeric μ-CN metal complexes [18–20], including the remarkable (and closely related) work of Höfler on cyano- and isocyanochromato complexes of the Group 12 metals [21], Vahrenkamp's novel μ_3-CN bonding mode [22] and Braunstein's topologically unique $Pd_4Mn_4(CN)_4$ cluster

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comprising two orthogonal μ-CN linked helices of opposite chirality [23].

With the aim of establishing the general accessibility and structural features of μ-cyano type supercomplexes we have now studied a complete series of pentacarbonyl(cyano)metalato complexes of Group 6–12 3d metals and complemented our work on Group 14 octahedro octahedra with an X-ray structural investigation of $(NEt_4)_2[Si\{NCCr(CO)_5\}_6]$ [14]. This communication reports the main results of these studies.

Syntheses

Unlike Behrens' tris{pentacarbonyl(cyano)chromato}chromium(III) [15] and Höfler's related tetracoordinated mercury(II) compound [21], both unexpected products from more complex reactions of $Br_2CNNCBr_2$ with $Cr(CO)_5^{2-}$ and $Hg\{NCCr(CO)_5\}_2$ with CN^-, respectively, all of our cyano-bridged coordination oligomers have been obtained by rather straightforward synthetic procedures. While the desired homoleptic hexacoordinated chromium(III) compound **4a** could be prepared from a chloro complex in dichloromethane in much the same way as the silicon, germanium and tin analogues **1a**–**3a** (eqns. (1) and (2), Scheme 1) [14], in other cases substitution of Cl^- by $[M(CN)(CO)_5]^-$ was not complete, giving rise only to heteroleptic complexes, e.g. $(NEt_4)_2[M(Cl)\{NCCr(CO)_5\}_3]$ ($M = Co^{II}$ (**7d**), Ni^{II} (**8d**)). We therefore switched to metal salts with the less strongly coordinating SO_4^{2-} or NO_3^- anions using deaerated water as a solvent. Reactions were then carried out with stoichiometric amounts of the water-soluble sodium salt of the 'ligand' immediately followed by the addition of NEt_4Br which caused the products to precipitate (eqn. (3)) (Scheme 1).

The new 'octahedro tetrahedra' synthesized that way in good to excellent yields are air-stable crystalline substances, all of which show increased thermal stabilities as compared to their mononuclear precursors (see Table 6). To our surprise, strikingly different substances were isolated from the reactions of $NiSO_4$ with $Na[M(CN)(CO)_5]$ (M = Cr, W), the red (cyanochromato)nickel species **8a** clearly belonging to the 'ot' class (see below) while the light-green tungstato derivative analyzed as the pentacoordinated $(NEt_4)_3[Ni\{NCW(CO)_5\}_5]$ (**8c**) (see Table 6). Our attempts to obtain supercomplexes with iron(III) or copper(II) as central atoms were unsuccessful; in both cases, complex formation occurred with simultaneous quantitative reduction of the metal salt to give the tetracoordinated Fe^{II} (**6a**) and tricoordinated (?) Cu^I complexes (**9**), respectively.

$$ECl_4,\ \text{resp.}\ K_2[SnCl_6] \xrightarrow[NEt_4Cl\ (-KCl)]{NEt_4[Cr(CN)(CO)_5]} (NEt_4)_2[E(NCCr(CO)_5)_6] \quad (1)$$

(E = Si (**1a**), Ge (**2a**), Sn (**3a**))

$$6\ NEt_4[Cr(CN)(CO)_5] + CrCl_3 \cdot 3THF \longrightarrow (NEt_4)_3[Cr(NCCr(CO)_5)_6] + 3\ NEt_4Cl \quad (2)$$

4a

$$Na[M'(CN)(CO)_5] \xrightarrow[(b)\ NEt_4Br]{(a)\ MSO_4,\ \text{resp.}\ Cr(NO_3)_3}$$

$$(NEt_4)_2[M(NCM'(CO)_5)_4]\ \text{resp.}\ (NEt_4)_3[Cr(NCM'(CO)_5)_6] \quad (3)$$

M' \ M	Cr	Mn	Fe	Co	Ni	Zn
Cr	4a	5a	6a	7a	8a	10a
Mo	4b	5b	6b	7b		10b
W	4c	5c	6c	7c	(8c)	10c

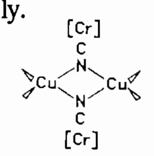
Scheme 1.

$(NEt_4)_3[Ni(NCW(CO)_5)_5]$

8c

$(NEt_4)_2[Cu(NCM'(CO)_5)_3]$

(M' = Cr (9a), W (9c))



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Concerning the latter, coordination number three, i.e. approximately trigonal-planar Cu^I species, is quite common among cyanocopper complexes, yet we are also aware of the pronounced tendency of Cu^I for tetrahedral coordination which is frequently achieved by ligand bridging [24]. Thus, as a structural alternative for **9** we tentatively suggest **11** which has its parallels in the cyanate bridging via N and, particularly, in the known μ_3-CN structures [25, 22, 26].

All complexes gave satisfactory C, H and N elemental analyses. For an unequivocal distinction between equally possible alternative stoichiometries, however, metal (M, M') analyses proved necessary, as in a number of cases the calculated values for C, H and N were almost identical. Electrolytic conductance measurements were carried out in 2.0×10^{-5} M solutions in acetone at 20 °C. All molar conductivities lie in the conductance ranges to be expected for the particular electrolyte type (see Table 6) [27].

During the preparation, IR spectroscopy was a most valuable tool to check if coordination had actually occurred (*vide infra*). In contrast, due to the rather limited solubility and stability in solution of the new compounds, ^{13}C NMR was not the method of choice, though a marked coordination effect showed up in the chemical shift of the cyano carbon atom on going from the free ligand $NEt_4[W(CN)(CO)_5]$ (δ (CD_2Cl_2) 201.0, 198.0 + ^{183}W satellites (CO_{trans}, CO_{cis} ($J = 125.4$ Hz)); 138.5 ppm (CN)) to the supercomplex $(NEt_4)_2[Zn\{NCW(CO)_5\}_4]$ (δ (CD_2Cl_2) 199.2, 196.6 + ^{183}W satellites (CO_{trans}, CO_{cis} ($J = 125.4$ Hz)); 149.9 ppm (CN)).

X-ray structures

All complex anions are thought to be composed of two types of idealized polygons, one comprising the set of (pseudo)octahedral 'monodentate ligands' which is arranged about the central metal in such a way that it generates the other. For a shorthand description of this topology in coordination compounds, we had earlier proposed the term 'octahedro octahedra' ('oo') which to some extent reflects the appropriate nomenclature [14]. A corresponding 'octahedro tetrahedron' ('ot') is depicted in Fig. 2. Note, however, that the MC_6 octahedra and the MN_4 tetrahedra have no common corners but are linked via (short) CN triple bonds.

Structure of $(NEt_4)_2[Co(Cl)\{NCCr(CO)_5\}_3]$ *(7d)*

Though to date no X-ray structure determination of a 'real' octahedro tetrahedron has been carried out, the above structural considerations are essentially borne out by the results which were obtained for the heteroleptic monochloro derivative **7d**. Figure 3 shows the stereochemistry of the complex anion which resides on a crystallographic mirror. Angles about the cobalt atom ranging from 107 to 114.5° are as expected for a moderately distorted tetrahedron in which the chlorine atom obviously is stereochemically more demanding than $[Cr(CN)(CO)_5]^-$ (!). According to this, the bends at the carbon (178(2), 175(2)°) and, more pronounced, at the nitrogen atoms of the μ-CN groups (175(2), 172(2)°) are such as to move the $Cr(CO)_5$ groups further away from the Cl (Table 1). We also note that one $Cr-C{\equiv}N-Co$ atomic sequence (the one lying on the mirror) is much less bent than the (symmetry-related) other two; very interestingly, the same 1:2 ratio of practically linear to strongly bent $M'-C{\equiv}N-M-N{\equiv}C-M'$ chains has recently been established for materials as different as the coordination polymer of the type of Prussian Blue, $[(R_3Sn)_3Co(CN)_6]_\infty$, and the salt-like $(NEt_4)_2[Si\{NCCr(CO)_5\}_6]$ (see below) containing discrete anionic octahedro octahedra [9]. Even in *mer*-$[Cr\{NCCr(CO)_5\}_3(THF)_3]$, the three Cr^0–CN–Cr^{III} bridges are nicely sorted out linear, nearly linear and slightly bent at the N atoms [15].

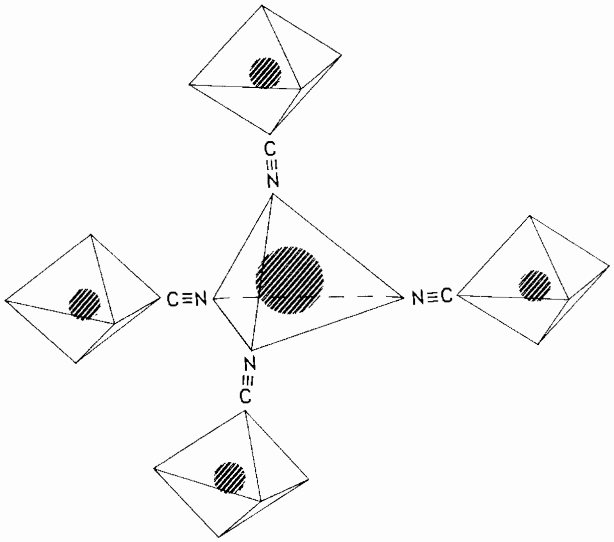

Fig. 2. Perspective drawing of an 'octahedro tetrahedron'.

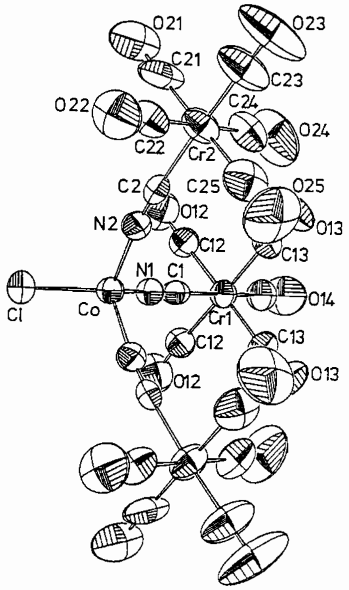

Fig. 3. ORTEP plot of the structure of the anion in $(NEt_4)_2[Co(Cl)\{NCCr(CO)_5\}_3]$ (**7d**) showing the thermal ellipsoids at the 30% probability level.

TABLE 1. Selected bond distances (Å) and angles (°) for **7d**[a]

Bond distances			
Co–N1	1.94(2)	N1–C1	1.15(4)
Co–N2	1.97(1)	N2–C2	1.12(2)
Co–Cl	2.23(1)		
Cr1–C1	2.07(3)		
Cr1–C12	1.86(2)	C12–O12	1.15(2)
Cr1–C13	1.90(2)	C13–O13	1.12(2)
Cr1–C14	1.82(4)	C14–O14	1.17(5)
Cr2–C2	2.04(1)		
Cr2–C21	1.80(2)	C21–O21	1.21(2)
Cr2–C22	1.88(3)	C22–O22	1.14(3)
Cr2–C23	1.83(2)	C23–O23	1.15(3)
Cr2–C24	1.89(3)	C24–O24	1.15(4)
Cr2–C25	1.92(2)	C25–O25	1.15(3)
Angles			
N1–Co–N2	107(1)	Co–N1–C1	175(2)
N1–Co–Cl	114(1)	Co–N2–C2	172(2)
N2–Co–Cl	110(1)	N1–C1–Cr1	178(2)
N2–Co–N2′	108(1)	N2–C2–Cr2	175(2)
C1–Cr1–C14	178(1)	C2–Cr2–C23	178(1)
C12–Cr1–C13	179(1)	C21–Cr2–C25	179(1)
		C22–Cr2–C24	178(1)
		Cr2–C21–O21	179(2)
Cr1–C12–O12	178(2)	Cr2–C22–O22	179(2)
Cr1–C13–O13	179(2)	Cr2–C23–O23	178(3)
Cr1–C14–O14	178(2)	Cr2–C24–O24	177(2)
		Cr2–C25–O25	179(2)

[a] e.s.d.s are given in parentheses.

Structure of $(NEt_4)_3[Ni\{NCW(CO)_5\}_5]$ (8c)

As already mentioned, nickel(II) salts react with $[Cr(CN)(CO)_5]^-$ to give the tetracoordinate supercomplexes **8a** and **8d**. The sudden formation of a five-coordinate species (**8c**) on changing to pentacarbonyl(cyano)tungstate as a ligand again sheds light on the chameleon-like ('anomalous') nature which nickel(II) consistently displays in coordination chemistry [28]. A particularly striking example of the flexibility of its coordination geometries has been found in the crystal structure of $[Cr(en)_3][Ni(CN)_5]$, in which approximately trigonal-bipyramidal pentacyanonickelate anions co-exist with perfectly square-pyramidal ones in the same unit cell [29]. This prompted us to elucidate the polyhedral shape of our $W(CO)_5$-stabilized penta-isocyanonickelate isomer in **8c** through an X-ray structure determination. A view of $[Ni\{NCW(CO)_5\}_5]^{3-}$ is given in Fig. 4. Table 2 provides a selection of bond lengths, bond angles and dihedral angles.

The poor quality of both X-ray structure analyses (particularly of the latter one) unfortunately precludes any detailed discussion of the bonding save for a note concerning the angles about μ-CN which again sweep from linear (Ni-N2-C2, Ni-N5-C5) via slightly bent (Ni-N3-C3) to strongly bent (Ni-N1-Cl, Ni-N4-C4). However, the structural deficiencies seem to point to what might be a more general problem with these kinds of huge ball-shaped supercomplexes, namely the impossibility to properly locate the peripheral ligands. In this respect, the CO envelope closely resembles the outer CH groups of the tetraalkylammonium cation, the high thermal motion of which adds to the overall structural uncertainties. Obviously, very little constraint is exercised on the ligands of the second coordination sphere much in contrast to the inner μ-CN groups which occupy well-defined positions between the metals. Hence, the $Ni(NCW)_5$ core is quite rigid, clearly approaching the 'exceptional form' of a square pyramid. While this is simply followed from inspection of Fig. 4, a quantitative measure of shape in such coordination compounds can be obtained from the dihedral angles formed by the normals to adjacent polytopal faces [30]. In Table 2, dihedral angles are presented for the NiN_5 polyhedron and for the two idealized polytopes for coordination number five with the 'shape determining angles' underlined. From there it is obvious that the 'δ criterion' requiring a dihedral angle pairing (δe_1 with δe_2 and δa_2 with δa_5) and the remaining angles to be

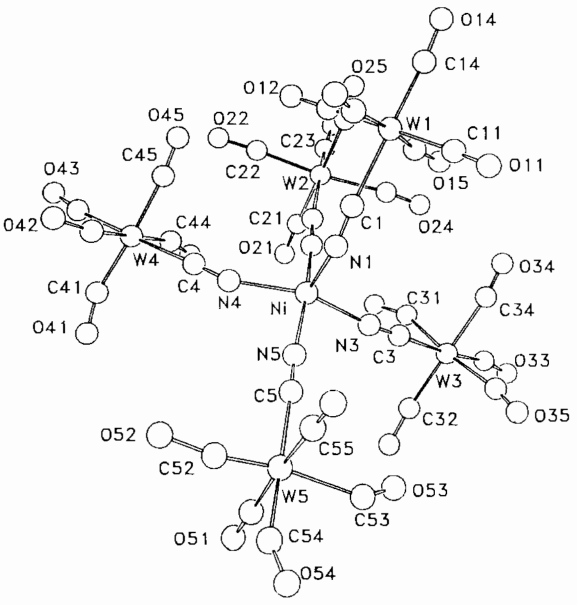

Fig. 4. Structure of the anion in $(NEt_4)_3[Ni\{NCW(CO)_5\}_5]$ (**8c**).

TABLE 2. Selected bond distances (Å), angles and dihedral angles (°) for **8c**[a]

Bond distances					
Ni–N1	1.94(3)		N1–C1		1.14(5)
Ni–N2	1.99(3)		N2–C2		1.17(5)
Ni–N3	2.05(3)		N3–C3		1.13(5)
Ni–N4	2.07(3)		N4–C4		1.11(4)
Ni–N5	2.03(3)		N5–C5		1.13(5)
C1–W1	2.21(4)				
C2–W2	2.19(4)				
C3–W3	2.16(4)				
C4–W4	2.19(3)				
C5–W5	2.18(4)				
Angles					
N1–Ni–N2	94(1)		N2–Ni–N3		87(1)
N1–Ni–N3	102(1)		N3–Ni–N5		90(1)
N1–Ni–N4	107(1)		N5–Ni–N4		90(1)
N1–Ni–N5	98(1)		N4–Ni–N2		87(1)
N2–Ni–N5	168(1)		N3–Ni–N4		151(1)
Ni–N1–C1	150(4)		W1–C1–N1		173(4)
Ni–N2–C2	178(3)		W2–C2–N2		175(3)
Ni–N3–C3	164(3)		W3–C3–N3		173(4)
Ni–N4–C4	156(3)		W4–C4–N4		171(3)
Ni–N5–C5	175(3)		W5–C5–N5		177(4)
Best planes					
I: N1, N3, N5		II: N1, N5, N4		III: N1, N4, N2	
IV: N1, N2, N3		V: N2, N3, N5		VI: N2, N5, N4	
Dihedral angles[b]					
I/II	80.8	II/III	$\underline{67.1}$	III/IV	$\underline{79.0}$
IV/I	$\underline{69.8}$	V/VI	$\underline{17.3}$	I/V	$\underline{127.1}$
IV/V	125.7	II/VI	129.7	III/VI	128.3
Ideal trigonal bipyramid[b]					
δa5	101.5	δe1	$\underline{53.1}$	δa2	101.5
δe2	$\underline{53.1}$	δe3	$\underline{53.1}$	δa6	101.5
δa3	101.5	δa4	101.5	δa1	101.5
Ideal tetragonal pyramid[b]					
δa5	75.7	δe1	$\underline{75.7}$	δa2	75.7
δe2	$\underline{75.7}$	δe3	$\underline{0.0}$	δa6	119.8
δa3	119.8	δa4	119.8	δa1	119.8

[a] e.s.d.s are given in parentheses. [b] cf. text and ref. 30.

equivalent is fulfilled by placing $[Ni\{NCW(CO)_5\}_5]^{3-}$ on the $D_{3h} \leftrightarrow C_{4v}$ geometric (Berry) reaction path, though much closer to the side of C_{4v}. Very similar conclusions are reached from simply sorting out the two largest N–Ni–N angles which differ by 17° as compared to the 60° and 0° expected for the limiting D_{3h} and C_{2v} polyhedra, respectively, or from a calculation of the mean deviations of the N–Ni–N angles from those of idealized models [31].

Structure of $(NEt_4)_2[Si\{NCCr(CO)_5\}_6]$ (1a)

A view of the 'oo' anion of **1a** is shown in Fig. 5 which also gives the atomic labeling system. Selected interatomic distances and angles appear in Table 3. The silicon atom is in the center of a rather distorted octahedron made up by six pseudooctahedral $NCCr(CO)_5$ groups, every two of which are symmetry-related by the crystallographic C_2 axis passing through Si. At least two findings about this structure deserve particular attention. One is hexacoordination about silicon which immediately has rarity value if one looks out for non-chelates [32]. It is therefore surprising that **1a** forms spontaneously, irrespective of the $SiCl_4$:$[Cr(CN)(CO)_5]^-$ stoichiometry used (cf. ref. 14). Still, we note the recent additions to the hexacoordinated silicon family, $[Si(NCS)_6]^{2-}$ and $[Si(NCSe)_6]^{2-}$, which, due to their isolobal nature are highly related to **1a** [33].

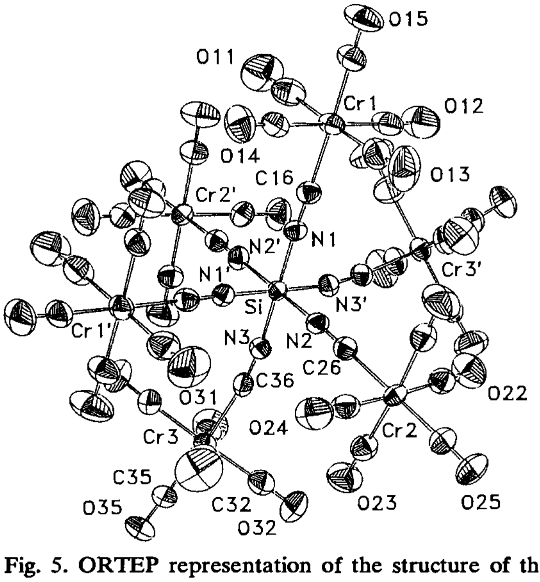

Fig. 5. ORTEP representation of the structure of the complex anion of **1a**. Probability ellipsoids are drawn at the 50% level.

TABLE 3. Selected bond distances (Å), angles and interplanar angles (°) for **1a**[a, b]

Bond distances			
Si–N1	1.827(3)	N1–C16	1.164(5)
Si–N2	1.800(3)	N2–C26	1.162(5)
Si–N3	1.817(3)	N3–C36	1.159(5)
Cr1–C11	1.918(5)	Cr3–C31	1.902(5)
Cr1–C12	1.905(5)	Cr3–C32	1.895(5)
Cr1–C13	1.890(5)	Cr3–C33	1.904(5)
Cr1–C14	1.889(4)	Cr3–C34	1.900(5)
Cr1–C15	1.874(4)	Cr3–C35	1.879(4)
Cr1–C16	2.033(4)	Cr3–C36	2.023(4)
Cr2–C21	1.893(4)		
Cr2–C22	1.891(4)		
Cr2–C23	1.899(4)	$C–O_{trans}$(av.)	1.137
Cr2–C24	1.888(4)	$C–O_{cis}$(av.)	1.137
Cr2–C25	1.891(4)		
Cr2–C26	2.007(4)		
Angles			
Si–N1–C16	177.3(3)	Cr1–C16–N1	178.9(3)
Si–N2–C26	172.8(3)	Cr2–C26–N2	176.6(3)
Si–N3–C36	168.5(3)	Cr3–C36–N3	171.1(3)
N1–Si–N2	89.6(1)	N2–Si–N1'	90.3(1)
N1–Si–N3	179.4(1)	N2–Si–N2'	179.8(2)
N1–Si–N1'	89.9(1)	N2–Si–N3	90.3(1)
N1–Si–N2'	90.3(1)	N3–Si–N1'	89.9(1)
N1–Si–N3'	89.9(1)	N3–Si–N2'	90.3(1)
N2–Si–N3	89.8(1)	N3–Si–N3'	90.2(1)

Best planes

I: N1', N2', N3', N2, Si	II: N1, N2, N3, N2', Si
III: N1, N3, N1', N3', Si	IV: C11, C12, C13, C14, Cr1
V: C11, C13, C15, C16, Cr1	VI: C12, C14, C15, C16, Cr1
VII: C21, C23, C25, C26, Cr2	VIII: C22, C24, C25, C26, Cr2
IX: C31, C32, C33, C34, Cr3	X: C31, C33, C35, C36, Cr3

Dihedral angles

I/II	89.9	I/III	89.6	II/III	89.6
I/IV	2.2	II/V	1.3	III/VI	0.5
II/VII	6.6	I/VIII	8.3	I/IX	27.4
II/X	47.6				

[a] e.s.d.s are given in parentheses. [b] Prime (') = (1 − x, y, 1.5 − z).

The other observation concerns the dramatic deviation from the expected linearity of the 11-atom sequence O≡C–Cr–C≡N–Si–N≡C–Cr–C≡O. Figure 6(a) features the *bc* plane with its large regularly shaped curvatures involving two thirds of the six Si–N–C–Cr vectors, while no such effect shows up in the *ab* and *ac* planes (Fig. 6(b)). These curvatures are the result of a cooperation of some severely bent angles at atoms originally thought to be sp-hybridized, viz., at N2 (Si–N2–C26 172.8(3)°), N3 (Si–N3–C36 168.5(3)°) and C36 (Cr3–C36–N3 171.1(3)°). Though this interesting phenomenon is frequently encountered in coordination oligomers and polymers of cyanometallates such as $K_2Zn_3[Fe(CN)_6]_2 \cdot H_2O$ [34a], $KCe(H_2O)_3[Fe(CN)_6] \cdot H_2O$ [34b], or the examples cited above, to date, the reasons for this are totally unclear; there is neither any special electronic effect — the Cr–C and C–N bond lengths (not the Si–N ones(!), cf., however, ref. 32) are behaving well (Table 3) — nor is there any obvious connection with crystal packing or hydrogen bonding.

A closer inspection of Fig. 5 supported by best planes-calculations unexpectedly reveals strictly eclipsed conformations of the Si–N (ligand) and $M–CO_{cis}$ bonds in

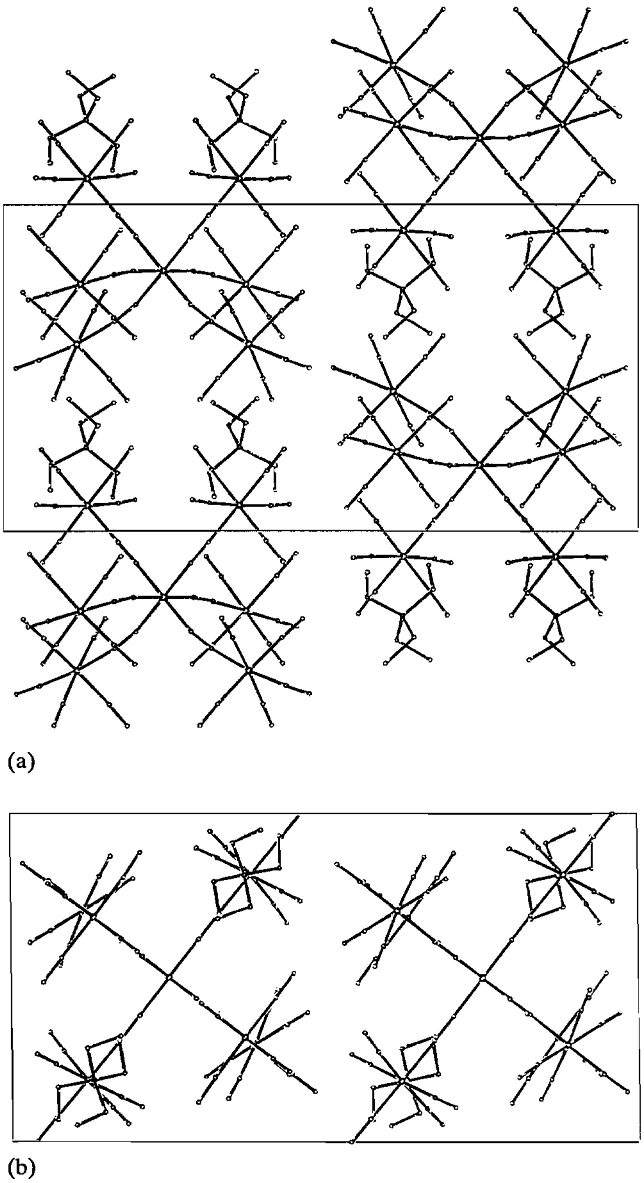

Fig. 6. Packing diagram of **1a** viewed down: (a) the *a* axis with *b* vertical and *c* horizontal; (b) the *b* axis with *a* vertical and *c* horizontal.

two of the three coordination planes, i.e. four out of six ligand octahedra have exactly the same orientation as the central one; only the coordination planes about Cr3 (IX, X (Table 3)) and, for symmetry reasons, those about Cr3′ deviate from the corresponding planes about silicon by 27.4 and 47.6°. Thus, ignoring non-linearity for a moment, we end up with an almost ideal overall O_h symmetry for the 'oo' species with possible implications for their vibrational spectra. Furthermore, these findings again point at the surprisingly low steric requirements of the complex ligands used (cf. discussion of structure of **7d**).

Vis–UV and IR spectra

Though most of the cyano-bridged octahedro polyhedra are coloured substances, none exhibits the intense colour expected for homo- or hetero-, di- or oligonuclear mixed-valence compounds. In view of the extremely different chemical environments of the two types of metals in these compounds, however, it is not surprising that no metal to metal-intervalence transition is observed. As a typical class I mixed valence-species [35], $(NEt_4)_3[Cr^{III}\{NCCr^0(CO)_5\}_6]$ (**4a**) thus has an electronic spectrum which appears to be a mere superposition of the spectra of the constituent ions $[Cr(CN)(CO)_5]^-$ and Cr^{III}(N-ligand)$_6$. While the high energy absorptions starting with a band at about 29 000 cm^{-1} (the obvious equivalent of the first spin-allowed $t_{2g}{}^6 \rightarrow t_{2g}{}^5 e_g{}^1$ transition at ~30 000 cm^{-1} of the parent hexacarbonyl [36]) clearly originate from the former, the latter acts as the chromophore giving rise to the lowest energy spectral feature which can be assigned as the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition. From its position, the Δ value can be taken directly, allowing to approximately locate the $[NCM(CO)_5]^-$ ligands in the spectrochemical series. There it lies towards the stronger end next to NCS$^-$ (cf. $\Delta([Cr(NCS)_6]^{3-}) = 17\,800$ cm^{-1} [37]) in excellent agreement with the isollobal relation $M(CO)_5 \leftarrow\!\!\circ\!\!\rightarrow S$ [38]. Analogous results have been obtained from an analysis of the electronic spectra of the tetrahedral Co^{II} complexes **7**, each of which displays two broad and structured d–d bands in the near-IR ($^4A_2 \rightarrow {}^4T_1(F)$, commonly denoted as ν_2) and visible region ($^4A_2 \rightarrow {}^4T_1(P)$, ν_3), respectively. From the energies of ν_2 and ν_3 almost identical values of Δ and B' have been calculated for **7a–c** using the equations of Tanabe and Sugano [39, 40a] (Table 4). Both ligand field parameters compare favorably to those of, for example, $[Co(NCS)_4]^{2-}$ ($\Delta(B') = 4550$ (691) cm^{-1}) [40b], $[Co\{N(CN)_2\}_4]^{2-}$ ($\Delta(B') = 4590$ (698) cm^{-1}) [41] and, particularly, $[Co(NCS)_4Hg]$ ($\Delta = 4880$ cm^{-1}) [40b].

The application of Jörgensen's 'average LF approximation' on the mixed-ligand complex $[Co(Cl)\{NCCr(CO)_5\}_3]^{2-}$ (**7d**) results in a perfect congruence between the predicted parameters and those calculated from ν_2 and ν_3 (Table 4) [37b].

A series of reflectance spectra was measured as a check for complex stability in solution. Allowing for their poor resolution, we can gather that in general there is no significant change in the complex ions upon dissolution in CH_2Cl_2. An exception is $[Ni\{NCW(CO)_5\}_5]^{3-}$ which dissolves in dichloromethane with change of colour from green to red. Much in contrast to the single broad spectral feature which appeared at about 27 000 cm^{-1} in the reflectance spectrum of **8c**, the solution spectrum shows two LF bands at exactly the same positions as the 'ot' (cyano-

TABLE 4. Electronic spectra of the complex ligands and selected supercomplexes (4500–40 000 cm^{-1})

Ion[a]	CH_2Cl_2 (cm^{-1}) (log ϵ_λ)	Solid (reflectance) (cm^{-1})	Δ (B') (cm^{-1})
$[Cr(CN)(CO)_5]^-$	29320 (3.85)		
$[Mo(CN)(CO)_5]^-$	39060 (5.28), 30300 (3.96), 28010 (4.04)		
$[W(CN)(CO)_5]^-$	39530 (5.29), 29590 (3.91), 27620 (4.04)		
$[Cr\{NCCr(CO)_5\}_6]^{3-}$	29070 (4.34), 19800sh, 18870 (2.23)	27780, 19380	18870
$[Cr\{NCMo(CO)_5\}_6]^{3-}$	39680 (5.36), 31060 (4.26), 28170 (4.24), 15150 (2.34)[b], 13930 (2.36)[b]	28570, 19680, 13660	
$[Cr\{NCW(CO)_5\}_6]^{3-}$	35090sh (4.48), 30210 (4.52), 28090 (4.46), 19120sh, 17950 (2.15)	27400, 18790, 13810	
$[Co\{NCCr(CO)_5\}_4]^{2-}$	29590 (4.20), 16450 (3.34), 8040 (2.47)	28570, 16560, 7810	4715 (690)
$[Co(Cl)\{NCCr(CO)_5\}_3]^{2-}$	29550 (4.01), 16070 (3.11), 7220 (2.10)		4190[c] (715)
$[Co\{NCMo(CO)_5\}_4]^{2-}$	33780 (4.22), 31250 (4.18), 28410 (4.21), 16670 (3.32), 8060 (2.41)	26320, 16450, 8010	4720 (705)
$[Co\{NCW(CO)_5\}_4]^{2-}$	35460sh (4.29), 30210 (4.20), 28010 (4.21), 16530 (3.34), 8060 (2.45)	27030, 16340, 8140	4725 (694)
$[Ni\{(NCCr(CO)_5\}_4]^{2-}$	30120 (4.13), 22420 (3.47), 10740 (1.70)	26670, 15150sh, 10840	
$[Ni\{NCW(CO)_5\}_5]^{3-}$	35210sh (4.43), 30300 (4.09), 28090 (4.11), 22780 (3.44), 10790 (1.70)	27030	

[a] Tetraethylammonium salts. [b] Bands are presumably due to decomposition. [c] Δ_{calc} ($=1/4\Delta([CoCl_4]^{2-})+3/4\Delta([Co\{NCCr(CO)_5\}_4]^{2-})$ refs. 37b, 40c) ≈ 4275 cm^{-1}.

chromato)nickel species **8a**. It is thus obvious that in solution one ligand complex dissociates from the five-coordinate nickel, a process which can be reversed by removing the solvent. Very remarkably, an identical behaviour has been reported of the system $Ni^{2+}/CN^-/K^+$ [42].

Characteristic IR and Raman data of the new complexes are given in Table 5. Those of the hexakis-{pentacarbonyl(cyano)chromato}silicon to -tin compounds including a $^{13}C(CN)$ labeled derivative (**1a′**) have already been discussed and are not included in Table 5 [14]. Unfortunately, some of the Raman spectra of the transition metal centered supercomplexes are of poor quality due to a partial decomposition in the laser beam of the coloured compounds. For the same reason, no Raman spectra could be obtained of the compounds **4**, **6c**, **7** and **8a**, nor are there any Raman spectra in solution where decomposition is especially rapid.

Throughout the synthetic work, the IR coordination shift $\Delta\nu(CN)=\nu(CN)_{complex}-\nu(CN)_{free\ ligand}$, served as the primary criterion of complex formation. Compared with $[M(CN)(CO)_5]^-$, in the supercomplexes the ν(CN) frequencies have moved to slightly higher values by some 5–30 cm^{-1} indicating the bridging function of the CN groups*. A shift to higher wavenumbers by the same order of magnitude is observed of the strongest ν(CO) band (E in terms of local symmetry) as a consequence of the lowering of the electron density at M′ on complexing the M^{n+} cations.

In the case of an overall T_d symmetry of the 'ot' complexes, three IR ($3T_2$) and six Raman active CO stretching vibrations ($2A_1+E+3T_2$) are calculated in addition to one IR (T_2) and two Raman active ν(CN)s (A_1+T_2). For local C_{4v} symmetry of the $M'(CO)_5$ fragments, three IR($2A_1+E$) and four Raman bands ($2A_1+B_2+E$) are to be expected. Though the actual 'ot' spectra seem to be more in agreement with the selection rules of a T_d model, a distinction cannot be made between the two vibrational models based solely on the data at hand.

However, the data unequivocally preclude any CN/NC coordination isomerism in our octahedro polyhedra, a phenomenon clearly established for $Hg\{NCCr(CO)_5\}_2$ from the occurrence of a second set of IR bands including high ν(CN) absorptions (~2200 cm^{-1}) [21].

We expected to get at least some information concerning the structure of the copper complexes from vibrational data (see above). Inspection of Table 5 shows that the ν(CN) frequencies of **9a**, **c** fall right into the narrow range spanned by the ν(CN) values of the μ_2-CN bridged species. At a first glance this seems to contradict the suggestion of a dimeric ligand-bridged (μ_3-CN) structure for **9**. For the isolobal NCO^- it has been pointed out, however, that bridges of this type, in principle, should not necessarily increase ν(CN) [43]. This is in fact observed in a number of (μ_2-NCO) complexes where bridging occurs via the cyanate nitrogen [25]. Furthermore we note a very 'normal' low ν(CN) value of the new μ_3-CN ($MnRu_2$) clusters [22].

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*The assignment of the highest band in the triple bond region to the ν(CN) mode has been substantiated by way of comparison with the respective features of $^{13}C(CN)$ labeled **1a′** (cf. ref. 14).

TABLE 5. Selected IR and Raman data

Ion[a]	IR (cm^{-1}) (CH_2Cl_2)		Raman (cm^{-1}) (solid)[c]	
	ν(CN)	ν(CO)	ν(CN)	ν(CO)
$[Cr(CN)(CO)_5]^{-}$	2095m	2053s, 1970w, 1923vs,br, 1890sh	2102s	2057m, 1974s, 1964sh, 1897w, 1879m
$[Mo(CN)(CO)_5]^{-}$	2097m	2059s, 1975w, 1927vs,br, 1895sh	2104m	2064m, 1973s, 1899w, 1876m, 1850w
$[W(CN)(CO)_5]^{-}$	2101m	2057s, 1965w, 1919vs,br, 1895sh	2109s	2063m, 1968vs, 1891w, 1874m
$[Cr\{NCCr(CO)_5\}_6]^{3-}$	2124m	2056s, 1989w, 1939vs,br, 1900sh	dec.[d]	
$[Cr\{NCMo(CO)_5\}_6]^{3-}$	2123w,br	2059s, 1985sh, 1929vs,br, 1895sh	dec.	
$[Cr\{NCW(CO)_5\}_6]^{3-}$	2128w,br	2070m, 2059s, 1983w, 1919vs,br, 1897sh	dec.	
$[Mn\{NCCr(CO)_5\}_4]^{2-}$	2108m	2051s, 1984w, 1940vs,br, 1910sh	2112w,br	2050w, 1977w, 1965–1900w, struct.
$[Mn\{NCMo(CO)_5\}_4]^{2-}$	2112m	2057s, 1986w, 1943vs,br, 1900sh	2119s, 2113s 2103m	2058vs, 2051s, 1990s, 1976vs, 1956m, 1927w, 1896w
$[Mn\{NCW(CO)_5\}_4]^{2-}$	2114m	2054s, 1978w, 1935vs,br, 1900sh	2119m	2054s, 1978w, 1955w, 1942–1871w, struct.
$[Fe\{NCCr(CO)_5\}_4]^{2-}$	2108m	2051s, 1985w, 1932vs,br, 1903sh	2113m	2048m, 1979m
$[Fe\{NCMo(CO)_5\}_4]^{2-}$	2111m	2056s, 1987w, 1943vs,br, 1910sh	2119s, 2113m	2057vs, 1992m, 1976s, 1957w, 1927w, 1913w, 1896w
$[Fe\{NCW(CO)_5\}_4]^{2-}$	2113m	2053s, 1979w, 1938vs,br, 1908sh	dec.[d]	
$[Co\{NCCr(CO)_5\}_4]^{2-}$	2116m	2053s, 1985w, 1940vs,br, 1912sh	dec.	
$[Co(Cl)\{NCCr(CO)_5\}_3]^{2-}$	2120m[b]	2051s, 1919vs,br[b]	dec.	
$[Co\{NCMo(CO)_5\}_4]^{2-}$	2119m	2058s, 1989w, 1943vs,br, 1910sh	dec.	
$[Co\{NCW(CO)_5\}_4]^{2-}$	2120m	2055s, 1980w, 1935vs,br, 1905sh	dec.	
$[Ni\{NCCr(CO)_5\}_4]^{2-}$	2124m,br	2054s, 1985w, 1940vs,br, 1910sh	dec.	
$[Ni(Cl)\{NCCr(CO)_5\}_3]^{2-}$	2126m[b]	2055s, 1939vs,br[b]		
$[Ni\{NCW(CO)_5\}_5]^{3-}$	2127m,br	2058s, 1975w, 1927vs,br, 1890sh	2136m, 2127m	2060s, 1999w, 1986w, 1969s, 1948w 1885w, 1875w
$[Ni\{NCW(CO)_5\}_5]^{3-}$	2136m, 2127m[b]	2069m, 2060s, 1900vs,br[b]		
$[Cu\{NCCr(CO)_5\}_3]^{2-}$	2124m,br	2055s, 1978sh, 1929vs,br, 1895sh	2121s, 2110s	2057m, 1975m, 1885w
$[Cu\{NCCr(CO)_5\}_3]^{2-}$	2119m, 2108w[b]	2054m, 1993m, 1915vs,br[b]		
$[Cu\{NCW(CO)_5\}_3]^{2-}$	2127m,br	2058s, 1975w, 1925vs,br, 1898sh		
$[Cu\{NCW(CO)_5\}_3]^{2-}$	2123m, 2112w[b]	2057s, 1900vs,br[b]		
$[Zn\{NCCr(CO)_5\}_4]^{2-}$	2124m	2056s, 1985w, 1940vs,br, 1912sh	2135m, 2127m	2055m, 1989sh, 1979s, 1934w, 1904w, 1895w
$[Zn\{NCMo(CO)_5\}_4]^{2-}$	2127m	2061s, 1988w, 1943vs,br, 1908sh	2139s, 2130s 2117w	2063s, 1992s, 1976vs, 1957m, 1946m 1927w, 1911m, 1896m
$[Zn\{NCW(CO)_5\}_4]^{2-}$	2128m	2059s, 1980w, 1936vs,br, 1905sh	2133m,br	2059m, 1975m, 1960–1890w, struct.

[a] Tetraethylammonium salts. [b] KBr pellets. [c] 'struct.' = band with pronounced structure. [d] Compound decomposed in the laser beam.

Mass spectra and thermogravimetrical measurements

Because of the thermal degradation of the complexes under electron impact conditions (see below), 'soft-ionization' via FAB(−) was used with the intention to observe the intact supercomplex anions within the matrix. In the first part of the study we investigated the free ligand complexes $[M'(CN)(CO)_5]^-$ (=A) (M′ = Cr, Mo, W) as tetraethylammonium salts (B^+). All complex anions (A) were detected in high amounts exhibiting the characteristic loss of CO. In the case of molybdenum, an increased formation of $[A-nCO]^-$ ions ($n = 1$–3) is noticed as compared to the chromium and tungsten complex analogues which is in agreement with the known substitution lability of $Mo(CO)_x$ systems.

Beside these mononuclear anions, two series of 'cluster ions' are observed, $(A,H,A)^-$ anions of low abundance and, with remarkable intensity, anions of the type $(A,B,A)^-$, both of which show distinct fragmentations. The low intensities of the former are in contradiction to their well established chemical existence; actually, a number of discrete CN–H–NC-bridged homo- and heterodinuclear complexes of a variety of metals has recently become available on a preparative scale [44]. No $(A,B,A)^-$ systems, on the other hand, are known to date.

The 'ot' supercomplexes **5a**, **b**, **6a**, **b**, **7a**, **b** and **10a**, **b** yield mixtures of three sets of species formed in matrix, A^-, $(MA_3)^-$ and $(MA_4, B)^-$, all of which show loss of CO; however, no further loss of ligands A nor of the counterion B is noticed from the complex fragments. In some cyanochromato complexes, ions with $m/z = (MA_3) + 78$ and $(MA_4, B) + 78$ are observed; the isotopic patterns of these species indicate that (CrCN) formed in the matrix by ligand decomposition has been added to the cluster ions.

In the spectra of the Cu^I supercomplexes **9a**, **c**, the monoanions $(A)^-$, $(CuA_2)^-$ and $(CuA_3,Cu)^-$ have been detected together with their specific fragmentation patterns. In an attempt to explain the formation of the dicopper ion, we also discuss the decomposition within the matrix of a possibly dimeric species (see above).

According to preliminary thermoanalytical studies, decomposition of the complexes of the homologous series $(NEt_4)_2[Co\{NCM'(CO)_5\}_4]$ (M′ = Cr, Mo, W) starts at about 100 °C and proceeds in roughly two steps with temperature ranges varying only slightly with M′ in the first step yet markedly in the second (M′ = Cr ($T_{onset} = 216$ °C), Mo (236 °C), W (252 °C)). Decomposition was completed at *c*. 400 °C at which temperature the mass loss amounted to 60–70%, the products analyzing as '$C_3CoM'_3N_3O_x$'. Similar results have been obtained with the zinc compounds **10**.

To get more insight into these pyrolyses, we have tried to correlate the DTA/TG data with the results of fractional evaporation of the complexes **7a** and **10a** at 20–450 °C under electron impact ionization [45]. The 'mass chromatograms' obtained that way show that at about 150 °C (1st step of TG/DTA) $[Cr(CO)_6]^+$ ions ($m/z = 220$) are almost exclusively formed from both types of complexes. Analysis by the 'Linked Scan' technique [46] of the metastable decomposition of *m/z* 220 further verifies that the main body of CO comes from this source. We then turned to the mass chromatograms of the ions with $m/z = 27$ and 28 which also displayed strongly temperature-dependent abundancies. As it was likely that these ions were mixtures of different elemental compositions, we have performed exact mass measurements which revealed that between 150 and 200 °C CO and HCN are preferentially formed (~80%), the former partly by extensive degradation of the first product of thermolysis, $Cr(CO)_6$, and partly by direct abstraction from the $NCCr(CO)_5$ ligands. At 270 °C, however, new ions ($C_2H_4^+$, $C_2H_3^+$, CH_2N^+) appear with high intensities indicating a rapid decomposition of NEt_4^+.

Final remarks and prospects

Clearly, additional work is necessary to arrive at a more detailed description of the ligand properties of NC[M′] and at a better understanding particularly of the structural ('$M'-C{\equiv}N-M-N{\equiv}C-M'$ non-linearity', NC[M′]-bridging?) and chemical implications ('induced reactivity' [13], 'catalytic activity') of linking metal systems via non-insulating CN bridges. It appears both attractive and promising to use the strategies outlined above to construct and design soluble homo- and hetero-oligomeric mixed-valence complexes with segments of Prussian Blue structures which are interesting in more than one respect. (For example, it has recently been shown that these originally purely inorganic solids can be modified to contain organometallic and organic sites with zeolithe-like properties [47].) In much the same way, using *trans*- or *cis*-dicyano complexes as ligands (e.g. $(NC)_2Mo(CO)_4^{2-}$ [48]) one ends up with chain- or layered-structures, respectively, reminding one of the beautiful work on coordination oligomers with rigid diisocyanides of Hanack on the one side and of Feinstein and Efraty on the other [49a, b]. Finally, coordination oligomers of the type described here with particularly reactive ligand sites, e.g. $NCFe(CO)_4^-$ [48], can be regarded as potential precursors to metal–metal bonded clusters.

Experimental

All operations were carried out in an inert gas atmosphere (usually Ar) using Schlenk tube techniques.

All solvents were deoxygenated with the organic solvents dried prior to use. UV–Vis–near-IR spectra were run on a Perkin-Elmer Lambda 9 (CH_2Cl_2 solution) and a Beckman 5270 instrument equipped with a standard reflectance attachment for powders. IR and Raman spectra were recorded on Perkin-Elmer 983 and SPEX RAMANLOG (Spectra Physics Kr- and Ar-ion lasers (647, 514.5 and 488 nm, respectively)) spectrometers. Electrolytic conductance measurements were carried out using a Metrohm Conductometer E518 and an EA 608-c cell calibrated with a 0.1 M aqueous solution of KBr. C, H, N and metal analyses were obtained with a Heraeus CHN-Rapid-Elementanalysator and a Philips SP 9 AAS. Melting points were taken on a Gallenkamp melting point apparatus and are uncorrected. FAB mass spectra were obtained with a CH5-DF Varian MAT (Bremen), Pyr-EI mass spectra with a MAT 711 Varian MAT (Bremen) instrument. ^{13}C NMR spectra were recorded on a Bruker AM 270, TG/DTA were run on a NETZSCH Simultane Thermoanalyseapparatur STA 409. $Na[Cr(CN)(CO)_5]$ and $NEt_4[Cr(CN)(CO)_5]$ were prepared by standard literature methods [50], $(NEt_4)_2[Si\{NCCr(CO)_5\}_6]$ (**1a**) and $(NEt_4)_2[Si\{N^{13}CCr(CO)_5\}_6]$ (**1a**′) as described previously [14].

Analytical data and physical properties of the new complexes are given in Table 6.

$(NEt_4)_2[Ge\{NCCr(CO)_5\}_6]$ (2a)

$GeCl_4$ (0.06 ml, 0.50 mmol) was added to a suspension of $Na[Cr(CN)(CO)_5]$ (0.73 g, 3.00 mmol) and NEt_4Cl (0.17 g, 1.00 mmol) in CH_2Cl_2 (160 ml), and the mixture was stirred overnight. The suspension was filtered, and the resulting yellow solution was concentrated to *c*. 25 ml. After a few days at −20 °C, yellow microcrystals of the product had formed which were filtered off, washed twice with n-pentane (5 ml) and dried *in vacuo* (0.15 g, 18% yield).

$(NEt_4)_2[Sn\{NCCr(CO)_5\}_6]$ (3a)

A suspension of $Na[Cr(CN)(CO)_5]$ (0.73 g, 3.00 mmol), $K_2[SnCl_6]$ (0.21 g, 0.50 mmol) and NEt_4Cl (0.17 g, 1.00 mmol) in a mixture of CH_2Cl_2 (50 ml) and methanol (1 ml) was allowed to stir at room temperature for 12 h, during which time the CH_2Cl_2 phase developed a yellow colour. Work-up as above yielded 0.13 g (15%) of **3a** as a yellow crystalline solid which like **2a** is soluble in methanol and acetone.

$(NEt_4)_3[Cr\{NCM'(CO)_5\}_6]$ (4a–c)

The same procedure was used as above with 8.0 mmol of $Na[M'(CN)(CO)_5]$ and 0.31 g (1.3 mmol) of $Cr(NO_3)_3$, but at a pH of 6 and with a longer period of stirring (12 h). Yields 55–65%.

4a has also been synthesized from $CrCl_3(THF)_3$ (0.16 g, 0.44 mmol) and $NEt_4[Cr(CN)(CO)_5]$ (1.04 g, 3.0 mmol) in dichloromethane (25 ml). After stirring for 14 h in the dark, the violet solution was filtered through a Celite pad on a coarse frit, and n-pentane was slowly added. At −20 °C, the complex separated as a violet powder which was dried *in high vacuo* and recrystallized from CH_2Cl_2/n-pentane to give 0.68 g (13%) of pure product.

General procedure for the preparation of the compounds $(NEt_4)_2[M^{II}\{NCM'(CO)_5\}_4]$ (5, 6, 7, 8a, 10) and $(NEt_4)_2[Cu\{NCM'(CO)_5\}_3]$ (9a, b)

8.0 mmol of $Na[M'(CN)(CO)_5]$ were dissolved in deoxygenated water (75 ml), and the pH was adjusted to ~1 by addition of 5 M H_2SO_4. To this solution, 2.0 mmol of solid MSO_4 were added with stirring. After 1 h of stirring, the crude reaction mixture was filtered directly into a saturated solution of tetraethylammonium bromide in water. The precipitate was filtered off, washed twice with water (10 ml) and dried *in vacuo*. Recrystallization from CH_2Cl_2 at −25 °C resulted in analytically pure air-stable compounds. Yield 65–90%.

An alternative synthesis of **6** starts out from $Fe_2(SO_4)_3$ (0.8 mmol) and $Na[M'(CN)(CO)_5]$ (8.0 mmol) applying the same conditions and work-up procedures as above.

$(NEt_4)_3[Ni\{NCW(CO)_5\}_5]$ (8c)

The procedure described above was applied using a 5:1 stoichiometric ratio of $Na[W(CN)(CO)_5]$ (1.30 g, 3.5 mmol) and $NiSO_4$ (0.11 g, 0.7 mmol) to yield 1.08 g (70%) of **8c**.

$(NEt_4)_2[Co(Cl)\{NCCr(CO)_5\}_3]$ (7d)

To a solution of 0.52 g (1.5 mmol) of $NEt_4[Cr(CN)(CO)_5]$ in 10 ml of CH_2Cl_2 was added solid $CoCl_2 \cdot 6H_2O$ (0.09 g, 0.37 mmol), and the mixture was allowed to stir at room temperature in the dark for 2 days. The solution was then dried (anhydrous Na_2SO_4), filtered and cooled to −25 °C. On addition of diethyl ether (7 ml) the product precipitated. Yield 0.08 g (21%).

$(NEt_4)_2[Ni(Cl)\{NCCr(CO)_5\}_3]$ (8d)

The same procedure was used as for **7d** with 1.40 g (4.02 mmol) of $NEt_4[Cr(CN)(CO)_5]$ in 30 ml of CH_2Cl_2 and 0.24 g (1.01 mmol) of $NiCl_2 \cdot 6H_2O$ in 6 ml of methanol. After the mixture was stirred for 12 h in the dark, the solvent was evaporated and the solid residue that resulted was redissolved in a minimum amount of CH_2Cl_2. Pure **8d** (0.27 g, 27%) was obtained by cooling this solution to −20 °C.

TABLE 6. Analytical and other data

Ion[a]	Molecular weight (g/mol)	Conductivity (S cm/mol)	Colour	Melting point (dec.)[b] (°C)	Analysis (%)					
						C	H	N	M	M′
$[Cr(CN)(CO)_5]^-$	$C_{14}H_{20}CrN_2O_5$	120	beige	97–98	(found)	47.99	5.72	7.84		
	348.36				(calc.)	48.27	5.80	8.04		
$[Mo(CN)(CO)_5]^-$	$C_{14}H_{20}MoN_2O_5$	123	colourless	102–103	(found)	42.58	5.05	7.21		
	392.30				(calc.)	42.86	5.15	7.14		
$[W(CN)(CO)_5]^-$	$C_{14}H_{20}N_2O_5W$	118	colourless	122–123	(found)	34.89	4.13	5.79		
	480.21				(calc.)	35.01	4.21	5.83		
$[Si\{N^{13}CCr(CO)_5\}_6]^{2-}$	$C_{52}H_{40}Cr_6N_8O_{30}Si$		colourless		(found)	39.30	2.64	6.95		
	1602.98				(calc.)	39.14	2.50	7.01		
$[Ge\{NCCr(CO)_5\}_6]^{2-}$	$C_{52}H_{40}Cr_6GeN_8O_{30}$	247	yellow	137–138	(found)	38.17	2.43	6.85		
	1641.48				(calc.)	38.05	2.46	6.83		
$[Sn\{NCCR(CO)_5\}_6]^{2-}$	$C_{52}H_{40}Cr_6N_8O_{30}Sn$	266	yellow	197–198	(found)	36.77	2.41	6.43		
	1687.58				(calc.)	37.01	2.39	6.64		
$[Cr\{NCCr(CO)_5\}_6]^{3-}$	$C_{60}H_{60}Cr_7N_9O_{30}$	340	red–violet	139–140	(found)	40.93	3.64	7.24	20.72(Cr)	
	1751.29				(calc.)	41.15	3.46	7.20	20.78	
$[Cr\{NCMo(CO)_5\}_6]^{3-}$	$C_{60}H_{60}CrMo_6N_9O_{30}$	338	red–violet	143–144	(found)	35.96	3.44	6.21		
	2014.93				(calc.)	35.76	3.01	6.26		
$[Cr\{NCW(CO)_5\}_6]^{3-}$	$C_{60}H_{60}CrN_9O_{30}W_6$	336	red–violet	148–149	(found)	28.79	2.85	4.95	2.26(Cr)	
	2542.39				(calc.)	28.34	2.38	4.96	2.04	
$[Mn\{NCCr(CO)_5\}_4]^{2-}$	$C_{40}H_{40}Cr_4MnN_6O_{20}$	239	colourless	118–120	(found)	40.33	3.57	6.92	4.55(Mn)	17.89(Cr)
	1187.80				(calc.)	40.44	3.40	7.08	4.62	17.51
$[Mn\{NCMo(CO)_5\}_4]^{2-}$	$C_{40}H_{40}MnMo_4N_6O_{20}$	236	beige	128–129	(found)	34.98	3.00	6.10	3.90(Mn)	
	1363.56				(calc.)	35.23	2.96	6.16	4.03	
$[Mn\{NCW(CO)_5\}_4]^{2-}$	$C_{40}H_{40}MnN_6O_{20}W_4$	243	beige	150–151	(found)	28.07	2.39	4.91	3.09(Mn)	
	1715.20				(calc.)	28.01	2.35	4.90	3.20	
$[Fe\{NCCr(CO)_5\}_4]^{2-}$	$C_{40}H_{40}Cr_4FeN_6O_{20}$	242	beige	125–126	(found)	40.35	3.47	7.12	4.79(Fe)	17.64(Cr)
	1188.71				(calc.)	40.41	3.40	7.07	4.70	17.50
$[Fe\{NCMo(CO)_5\}_4]^{2-}$	$C_{40}H_{40}FeMo_4N_6O_{20}$	244	beige	132–133	(found)	34.90	3.00	6.14	4.00(Fe)	
	1364.47				(calc.)	35.21	2.96	6.16	4.09	
$[Fe\{NCW(CO)_5\}_4]^{2-}$	$C_{40}H_{40}FeN_6O_{20}W_4$	247	colourless	154–155	(found)	27.79	2.40	4.84	2.87(Fe)	
	1716.11				(calc.)	27.99	2.35	4.90	3.25	
$[Co\{NCCr(CO)_5\}_4]^{2-}$	$C_{40}H_{40}CoCr_4N_6O_{20}$	239	green	137–138	(found)	40.04	3.44	6.87	5.30(Co)	17.55(Cr)
	1191.79				(calc.)	40.31	3.39	7.05	4.94	17.45
$[Co(Cl)\{NCCr(CO)_5\}_3]^{2-}$	$C_{34}H_{40}ClCoCr_3N_5O_{15}$		green	123–124	(found)	40.46	4.06	6.75		
	1009.17				(calc.)	40.45	3.96	6.94		
$[Co\{NCMo(CO)_5\}_4]^{2-}$	$C_{40}H_{40}CoMo_4N_6O_{20}$	245	green	138–139	(found)	34.96	2.96	6.07	4.20(Co)	
	1367.55				(calc.)	35.13	2.95	6.15	4.31	
$[Co\{NCW(CO)_5\}_4]^{2-}$	$C_{40}H_{40}CoN_6O_{20}W_4$	231	green	153–155	(found)	28.10	2.40	4.94	3.08(Co)	
	1719.19				(calc.)	27.94	2.35	4.89	3.43	
$[Ni\{NCCr(CO)_5\}_4]^{2-}$	$C_{40}H_{40}Cr_4N_6NiO_{20}$	244	red	103–105	(found)	40.10	3.83	6.79	4.57(Ni)	17.14(Cr)
	1191.55				(calc.)	40.32	3.39	7.05	4.92	17.46
$[Ni(Cl)\{NCCr(CO)_5\}_3]^{2-}$	$C_{34}H_{40}ClCr_3N_5NiO_{15}$		red	118–119	(found)	40.25	4.16	6.75	5.94(Ni)	15.30(Cr)
	1008.84				(calc.)	40.48	4.00	6.94	5.82	15.46
$[Ni\{NCW(CO)_5\}_5]^{3-}$	$C_{54}H_{60}N_8NiO_{25}W_5$	334	light-green	115–116	(found)	29.48	2.80	5.09	2.61(Ni)	
	2199.16				(calc.)	29.49	2.76	5.10	2.67	
$[Cu\{NCCr(CO)_5\}_3]^{2-}$	$C_{34}H_{40}Cr_3CuN_5O_{15}$	202	colourless	102–103	(found)	41.69	4.16	7.21	6.63(Cu)	15.63(Cr)
	978.34				(calc.)	41.74	4.13	7.16	6.50	15.94
$[Cu\{NCW(CO)_5\}_3]^{2-}$	$C_{34}H_{40}CuN_5O_{15}W_3$	207	beige	114–115	(found)	29.50	2.90	5.13	4.86(Cu)	
	1373.89				(calc.)	29.72	2.94	5.10	4.62	
$[Zn\{NCCr(CO)_5\}_4]^{2-}$	$C_{40}H_{40}Cr_4N_6O_{20}Zn$	240	colourless	129–130	(found)	39.76	3.58	6.82	5.61(Zn)	16.97(Cr)
	1198.25				(calc.)	40.09	3.37	7.01	5.46	17.36
$[Zn\{NCMo(CO)_5\}_4]^{2-}$	$C_{40}H_{40}Mo_4N_6O_{20}Zn$	237	beige	118–119	(found)	34.59	3.01	6.05	4.75(Zn)	
	1374.01				(calc.)	34.96	2.94	6.12	4.76	
$[Zn\{NCW(CO)_5\}_4]^{2-}$	$C_{40}H_{40}N_6O_{20}W_4Zn$	235	beige	143–145	(found)	27.82	2.54	5.19	4.08(Zn)	
	1725.65				(calc.)	27.84	2.34	4.87	3.79	

[a] Tetraethylammonium salts. [b] All complexes melt with decomposition.

X-ray crystal structure determinations

Single crystals of **1a** and **8c** were grown by cooling saturated solutions in CH_2Cl_2, those of **7d** by layering a CH_2Cl_2 solution with diethyl ether. Crystals of suitable size were mounted under argon in glass capillaries. All crystallographic data were collected on a STOE four circle-diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Unit cell parameters were obtained by a least-squares refinement of the angular settings from 25 reflections, well distributed in reciprocal space and lying in a 2θ range of 20–30°. Crystallographic data are given in Table 7.

All data were corrected for Lorentz–polarization effects during the final stages of data reduction. An absorption correction was carried out for **8c**. All structures were solved by employing a combination of direct methods and difference Fourier techniques with scattering factors for neutral atoms taken from the literature [51]. All the crystallographic computations were carried out on a VAX computer using the programs listed in Table 7. After all of the non-hydrogen atoms were located and refined, the hydrogen atoms of the cation of **1a** were placed in positions suggested by the difference Fourier maps. Final refinement included anisotropic thermal parameters for all non-hydrogen atoms and isotropic ones for the hydrogen atoms (**1a**). The full matrix least-squares refinement was based on F, and the function minimized was $\Sigma\omega(|F_o|-|F_c|)^2$. Agreement factors are defined as $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $R_w=[\Sigma(w||F_o|-|F_c||^2)/\Sigma(w|F_o|^2)]^{1/2}$, $w=1/\{\sigma(F_o)\}^2$.

The rather high R values in **7d** are attributed partly to a considerable disorder of the tetraethylammonium groups, particularly of their peripheric carbon atoms, partly to four maxima of residual electron density in the difference Fourier maps near the position 0.0, 0.0, 0.68. These peaks are at distances of only ~1.5 Å to one another, yet there are no close contacts to other atoms. They obviously belong to a solvent molecule, though an attempted refinement as atoms of diethyl ether with low occupancy was unsuccessful.

Unlike in **7d**, the reason for the unsatisfactory R values and standard deviations in the structure of **8c** clearly lies in the low scattering power of the crystals. Thus, of the 8248 diffraction data originally collected in the 2θ range of 2–54°, 3897 had intensities $<2\sigma(F)$. We therefore decided to restrict ourselves to the reflections (5994) in the range of 2–38° of which, however, still 1843 were unobserved. We explain the generally low scattering ability of the crystals of this kind of compound with a lack of order of the light atoms, in particular of the outer CH groups of the tetraethylammonium cations (and the carbonyl oxygen atoms of

TABLE 7. Crystallographic data collection parameters

	1a	**7d**	**8c**
Crystal data			
Formula	$C_{52}H_{40}Cr_6N_8O_{30}Si$	$C_{34}H_{40}ClCoCr_3N_5O_{15}$	$C_{54}H_{60}N_8NiO_{25}W_5$
Molecular weight (g/mol)	1596.98	1009.17	2199.16
Crystal size (mm)	0.50×0.25×0.32	1.00×0.90×0.50	0.50×0.20×0.32
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2/c$	$C2/m$	$P2_1/n$
Cell parameters			
a (Å)	12.363(3)	18.204(9)	16.222(4)
b (Å)	12.291(4)	18.889(7)	20.299(8)
c (Å)	23.581(3)	17.58(1)	22.982(5)
β (°)	90.69(4)	119.28(3)	103.63(2)
U (Å^3)	3581.6	5272.7	7354.6
Z	2	4	4
D_c (g cm^{-3})	1.480	1.185	1.992
Collection and refinement parameters			
Radiation (λ (Å))	graphite-monochromated Mo Kα (0.7107)		
μ (cm^{-1})	9.80	9.87	85.82
Temperature (K)	293	293	293
Scan mode	ω-scan	ω-scan	ω-scan
2θ Limits (°)	$4\leqslant 2\theta\leqslant 50$	$4\leqslant 2\theta\leqslant 50$	$4\leqslant 2\theta\leqslant 50$
Total no. reflections	6147	4821	5994
No. data ($I\geqslant 2\sigma(I)$)	4221	2622	4151
No. parameters	520	333	453
R	0.050	0.100	0.098
R_w	0.035	0.093	0.064
Programs used	MULTAN 77 X-Ray 76	SHELXS-86 XTAL 2.2 DIFABS	SHELXS-86 XTAL 2.2 DIFABS

the complex anions, see text above), and this is supported by the observed high temperature factors.

Supplementary material

For **7d**, **8c** and **1a**, Tables 8–12 of atomic coordinates and anisotropic thermal parameters (including coordinates and isotropic temperature factors for the hydrogen atoms of **1a**); listings of observed and calculated structure factors for all observed reflections; a figure (Fig. 7) showing the atomic numbering scheme for the NEt_4^+ cation in **1a**; Table 13 of interionic distances in **1a**, and complete NI-FAB spectra may be obtained from the authors on request.

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References

1 A. G. Sharpe, *The Chemistry of Cyano Complexes of the Transition Metals,* Academic Press, London, 1976.

2 W. Beck and W. P. Fehlhammer, in H. J. Emeléus, C. C. Addison and D. B. Sowerby (eds.), *MTP International Review of Science, Inorg. Chem. Ser. I,* Vol. 2, Butterworths, London, 1972, p. 253, and refs. therein.

3 E. Bär, A. Völkl, F. Beck, W. P. Fehlhammer and A. Robert, *J. Chem. Soc., Dalton Trans.,* (1986) 863.

4 E. Bär and W. P. Fehlhammer, *J. Organomet. Chem., 353* (1988) 197.

5 D. Rieger, F. E. Hahn and W. P. Fehlhammer, *J. Chem. Soc., Chem. Commun.,* (1990) 285.

6 M. Schaal, W. Weigand, U. Nagel and W. Beck, *Chem. Ber., 118* (1985) 2186.

7 I. Hashimoto, N. Tsuruta, M. Ryang and S. Tsutsumi, *J. Org. Chem., 35* (1970) 3748; T. Funabiki, S. Yoshida and K. Tarama, *J. Chem. Soc., Chem. Commun.,* (1978) 1059.

8 P. Brandt, R. D. Fischer, E. S. Martinez and R. Diaz Calleja, *Angew. Chem., Int. Ed. Engl., 28* (1989) 1265.

9 M. Adam, A. K. Brimah, R. D. Fischer and L. Xing-Fu, *Inorg. Chem., 29* (1990) 1595.

10 D. Gaswick and A. Haim, *J. Inorg. Nucl. Chem., 40* (1978) 437; A. Burewicz and A. Haim, *Inorg. Chem., 27* (1988) 1611.

11 A. Vogler, A. H. Osman and H. Kunkely, *Coord. Chem. Rev., 64* (1985) 159; *Inorg. Chem., 26* (1987) 2337.

12 G. A. Carriedo, N. G. Connelly, M. C. Crespo, I. C. Quarmby and V. Riera, *J. Chem. Soc., Chem. Commun.,* (1987) 1806; G. A. Carriedo, N. G. Connelly, M. C. Crespo, I. C. Quarmby, V. Riera and G. H. Worth, *J. Chem. Soc., Dalton Trans.,* (1991) 315.

13 A. Christofides, N. G. Connelly, H. J. Lawson and A. C. Loyns, *J. Chem. Soc., Chem. Commun.,* (1990) 597.

14 E. Bär, W. P. Fehlhammer, D. K. Breitinger and J. Mink, *Inorg. Chim. Acta, 82* (1984) L17.

15 F. Edelmann and U. Behrens, *J. Organomet. Chem., 131* (1977) 65.

16 H. Siebert, *Z. Anorg. Allg. Chem., 327* (1964) 63.

17 B. L. Shaw and G. Shaw, *J. Chem. Soc. A,* (1971) 3533; R. F. Phillips and H. M. Powell, *Proc. R. Soc. London, 173* (1939) 147.

18 J. A. Davies, F. R. Hartley, S. G. Murray and M. A. Pierce-Butler, *J. Chem. Soc., Dalton Trans.,* (1983) 1305.

19 H. C. Aspinall, A. J. Deeming and S. Donovan-Mtunzi, *J. Chem. Soc., Dalton Trans.,* (1983) 2669.

20 A. J. Deeming, G. P. Proud, H. M. Dawes and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.,* (1988) 2475; A. J. Deeming, G. P. Proud, H. M. Dawes and M. B. Hursthouse, *Polyhedron, 7* (1988) 651.

21 M. Höfler, W. Jung, M. Scobel and J. Rademacher, *Chem. Ber., 119* (1986) 3268.

22 B. Oswald, A. K. Powell, F. Rashwan, J. Heinze and H. Vahrenkamp, *Chem. Ber., 123* (1990) 243.

23 P. Braunstein, B. Oswald, A. Tiripicchio and M. Tiripicchio Camellini, *Angew. Chem., Int. Ed. Engl., 29* (1990) 1140.

24 A. F. Wells, *Structural Inorganic Chemistry,* Clarendon, Oxford, 5th edn., 1984, p. 1107f.

25 A. M. Golub, H. Köhler and V. V. Skopenko, *Chemistry of Pseudohalides,* Elsevier, Amsterdam, 1986, p. 212f.

26 D. T. Cromer, A. C. Larson and R. B. Roof, Jr., *Acta Crystallogr., 19* (1965) 192.

27 W. J. Geary, *Coord. Chem. Rev., 7* (1971) 81.

28 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry,* Wiley, New York, 4th edn., 1980, p. 783f.

29 K. N. Raymond, P. W. R. Corfield and J. A. Ibers, *Inorg. Chem., 7* (1968) 1362.

30 E. L. Muetterties and L. J. Guggenberger, *J. Am. Chem. Soc., 96* (1974) 1748.

31 A. Schmuck and K. Seppelt, *Chem. Ber., 122* (1989) 803; U. Engelhardt and C. Renz-Kreikebohm, *Acta Crystallogr., Sect. C, 45* (1989) 1679.

32 S. N. Tandura, M. G. Voronkov and N. V. Alekseev, *Top. Curr. Chem., 131* (1986) 99.

33 W. Heininger, R. Stucka and G. Nagorsen, *Z. Naturforsch., Teil B, 41* (1986) 702; W. Heininger, K. Polborn and G. Nagorsen, *Z. Naturforsch., Teil B, 43* (1988) 857.

34 (a) P. Gravereau, E. Garnier and A. Hardy, *Acta Crystallogr., Sect. B, 35* (1979) 2843; (b) D. F. Mullica, W. O. Milligan and J. D. Oliver, *Inorg. Nucl. Chem. Lett., 15* (1979) 1.

35 D. F. Shriver, P. W. Atkins and C. H. Langford, *Inorganic Chemistry,* Oxford University Press, Oxford, 1990, pp. 460–461; M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem., 10* (1967) 247; D. B. Brown (ed.), *Mixed Valence Compounds,* Reidel, Dordrecht, 1980.

36 G. L. Geoffroy and M. S. Wrighton, *Organometallic Photochemistry,* Academic Press, New York, 1979.

37 (a) C. K. Jørgensen, *Oxidation Numbers and Oxidation States,* Springer, Berlin 1969; (b) *Absorption Spectra and Chemical Bonding in Complexes,* Pergamon, Oxford, 1964.

38 J. E. Ellis, *J. Organomet. Chem., 86* (1975) 1.

39 Y. Tanabe and S. Sugano, *J. Phys. Soc. Jpn., 9* (1954) 753.

40 (a) F. A. Cotton and M. Goodgame, *J. Am. Chem. Soc., 83* (1961) 1777; (b) F. A. Cotton, D. M. L. Goodgame, M. Goodgame and A. Sacco, *J. Am. Chem. Soc., 83* (1961) 4157;

(c) F. A. Cotton, D. M. L. Goodgame and M. Goodgame, *J. Am. Chem. Soc., 83* (1961) 4690.

41 H. Köhler and B. Seifert, *Z. Anorg. Allg. Chem., 344* (1966) 63.

42 L. Sacconi, F. Mani and A. Bencini, in G. Wilkinson, R. D. Gillard and J. A. McCleverty (eds.), *Comprehensive Coordination Chemistry,* Vol. 5, Pergamon, Oxford, 1987, p. 68f.

43 A. Yu. Tsivadze, G. V. Tsintsadze, Yu. Ya. Kharitonov, A. M. Golub and A. M. Mamulashvili, *Russ. J. Inorg. Chem., 15* (1970) 934.

44 E. Bär, J. Fuchs, D. Rieger, F. Aguilar-Parrilla, H.-H. Limbach and W. P. Fehlhammer, *Angew. Chem., Int. Ed. Engl., 30* (1991) 88.

45 G. Holzmann and C. Leuckert, *Phytochemistry, 29* (1990) 2277, and refs. therein.

46 A. F. Weston, K. R. Jennings, S. Evans and R. M. Elliott, *Int. J. Mass Spectrom. Ion Phys., 20* (1976) 317; G. Holzmann and G. Kossmehl, *Org. Mass Spectrom., 15* (1980) 336, and refs. therein.

47 P. Brandt, A. K. Brimah and R. D. Fischer, *Angew. Chem., Int. Ed. Engl., 27* (1988) 1521.

48 M. Fritz, G. Holzmann and W. P. Fehlhammer, unpublished results.

49 (a) U. Keppeler, O. Schneider, W. Stöffler and M. Hanack, *Tetrahedron Lett., 25* (1984) 3679; U. Keppeler and M. Hanack, *Chem. Ber., 119* (1986) 3363; S. Deger and M. Hanack, *Synth. Met., 13* (1986) 319; (b) A. Efraty, I. Feinstein and F. Frolow, *Inorg. Chem., 21* (1982) 485; I. Feinstein-Jaffe, F. Frolow, L. Wackerle, A. Goldman and A. Efraty, *J. Chem. Soc., Dalton Trans.,* (1988) 469.

50 W. P. Fehlhammer, W. A. Herrmann and K. Öfele, in G. Brauer (ed.), *Handbuch der Präparativen Anorganischen Chemie,* Vol. III, Ferdinand Enke, Stuttgart, 3rd edn., 1981.

51 D. T. Cromer and J. T. Waber, *International Tables for X-ray Crystallography,* Vol. IV, Kynoch, Birmingham, UK, 1974, p. 99.