Cyanide-Bridged Oligonuclear Complexes Containing Ni-CN-Cu and Pt-CN-Cu Linkages

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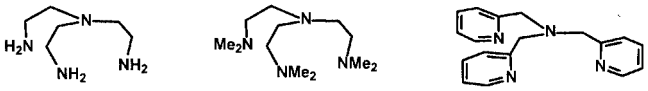
The central building blocks $Ni(CN)_4^{2-}$ and $Pt(CN)_4^{2-}$ can be combined with one, two or four $Cu^{II}L$ units (L = tren, Me_6tren, tpa) to form di-, tri- and pentanuclear complexes with Ni-CN-Cu and Pt-CN-Cu linkages. Structure determinations of these and the side product [(tren)-Cu–CN–Cu(tren)] $(ClO_4)_2$ reveal mostly linear M-C-N-Cu arrays and *cis*-, *trans*- and star-like arrangements of the CN-Cu units around the central Ni or Pt ions. The $\tilde{\nu}$(CN) IR data for the bridging cyanides show a characteristic hypsochromic effect compared to the data for the free $M(CN)_4^{2-}$ complexes. The absorption bands in the visible spectra of the oligonuclear complexes are shifted to shorter wavelengths than those of the free LCu^{II}-X complexes. The Cu^{II}/Cu^{I} redox steps in the cyclic voltammograms allow the conclusion that there is electronic communication between the external CuL units when they are arranged in a *trans*-orientation at Pt^{II}, but not Ni^{II}, centers.

Introduction

In a series of papers[1–6] and a review article[7] we have outlined and justified our research work on cyanide-bridged oligonuclear complexes with chain-like arrangements of metal ions and cyanide ligands. This work, which has also been pursued by the research groups of Haim,[8] Connelly,[9] Vogler,[10] Scandola[11] and Denning,[12] originates from the observation that a bridging cyanide is a good conductor of electronic interactions between the metallic groups attached to it. In this context it is not so much the bulk properties like magnetism, luminescence or electrical conductivity that interest us, but the phenomena which result from metal-metal charge transfer like multi-redox steps, mixed valence and long-range electronic interactions.

For this purpose we have synthesized a series of compounds in which the number of cyanide-bridged metal atoms, their ligation patterns and redox properties, the orientation of the bridging ligand (CN versus NC) and the geometry at the interconnected metal atoms (cis, trans, tetrahedral, square planar, octahedral) have been varied. So far we, like others, have been unable to fully characterize chains with more than three CN-linked metal atoms. The best, though not the only, arrangement for long-range metal-metal interactions was found in trans-configured central $M(CN)_2$ or $M(NC)_2$ units derived from square-planar L_2MX_2 or octahedral L_4MX_2 building blocks. Of these, linear arrays M′(μ-CN)Pt(μ-CN)M′ of organometallic L_nM' units attached to $Pt(CN)_2$ centers were the best objects of study due to their inertness and favourable redox properties.[2]

Based on this we have focused our synthetic work on the complexes $[Pt(CN)_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ as starting materials, to which various external redox-active complex units were to be attached. For the present work we chose copper-containing external units in which copper is in a trigonal-bipyramidal ligand environment due to the fact that both Cu^{I} and Cu^{II} are reasonably stable in this environment. The uncharged tripodal ligands tren, Me_6tren and tpa were used to support the trigonal bipyramidal geometry at copper. While the main purpose of the work was to study linear Cu-NC-Ni-CN-Cu and Cu-NC-Pt-CN-Cu arrays, we were also interested in finding out whether all possible modes of attachment of the copper units to the $M(CN)_4$ centers (one to four such units and cis or trans arrays for two of them) could be realized.



tren Me_6tren tpa

Results and Discussion

$Ni(CN)_4$-Centered Complexes

The first experiments in this series yielded an unexpected result: when $(PPN)_2[Ni(CN)_4]$ was treated with four equiva-

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lents of $[Cu(tren)H_2O](ClO_4)_2$ in dimethylformamide, cyanide transfer occurred and the dicopper complex **1** was obtained. It turned out that cyanide transfer is a common feature in these compounds, and could be avoided by using not too polar solvents. Complex **1** with PF_6 counterions has already been described, but not structurally characterized.[13] In addition, the analogous complexes with Me_3tren and Me_6tren ligands have been fully characterized.[14,15]

$$[(tren)Cu-CN-Cu(tren)](ClO_4)_3$$
1

Compound **1** can be considered a reference compound here for structural and spectroscopic comparisons. Its $\tilde{\nu}$(CN) IR absorptions (2182 and 2163 cm^{-1} in KBr) occur at the upper end of the frequency range of all copper compounds described here, and they are also higher than all other reported values for dinuclear M-CN-M′ complexes with organometallic constituents.[1] This means that the $(tren)Cu^{II}$ unit at the C terminus of the cyanide (the only such unit in this paper) is a very poor π-backdonator. The fact that two $\tilde{\nu}$(CN) bands are observed is explained by the existence of two independent complex units in the asymmetric unit of the crystals' unit cell (see below). The spread of the two bands for identical species may serve as a caveat against too detailed discussions of $\tilde{\nu}$(CN) variations in such complexes.

The intended attachment of two L·Cu units to the $Ni(CN)_4$ center could be achieved by adjusting the conditions for (tren)Cu, (Me_6tren)Cu and (tpa)Cu. All three resulting complexes **2**, **3** and **4** were obtained as *trans*-$Ni(CN)_2X_2$ species, i.e. they contain the linear Cu-NC-Ni-CN-Cu arrays. In one case, however, the use of $K_2[Ni(CN)_4]$ instead of $(PPN)_2[Ni(CN)_4]$, and a slight variation of the reaction conditions, yielded a small amount of the *cis*-oriented complex **5**. In contrast to all other new compounds in this paper, which are blue, **5** is blue-green. In one case, namely for L·Cu = (tpa)Cu, the attachment of four L·Cu units was possible: $(PPN)_2[Ni(CN)_4]$ and four equivalents of $[Cu(tpa)CH_3CN](ClO_4)_2$ yielded the pentanuclear complex **6**.

trans-$[L{\cdot}Cu\text{-}NC\text{-}Ni(CN)_2\text{-}CN\text{-}Cu{\cdot}L](ClO_4)_2$
2: L = tren; **3**: L = Me_6tren; **4**: L = tpa

cis-$[(tpa)Cu\text{-}NC\text{-}Ni(CN)_2\text{-}CN\text{-}Cu(tpa)](ClO_4)_2$
5

$[Ni\{CN\text{-}Cu(tpa)\}_4](ClO_4)_6$
6

$Pt(CN)_4$-Centered Complexes

The chemistry of the $Pt(CN)_4$-centered complexes was not fully analogous to that of the $Ni(CN)_4$-centered ones. For platinum the attachment of only one L·Cu unit was possible, resulting in the dinuclear complex **7**. Complex **7** corresponds to several such dinuclear complexes obtained from $L_2Pt(CN)_2$ species and organometallic building blocks. Its low symmetry is reflected by the occurrence of four $\tilde{\nu}$(CN) bands (see Exp. Sect.) of which the highest one at 2179 cm^{-1} can be assigned to the bridging cyanide.

$$[(tpa)Cu\text{-}NC\text{-}Pt(CN)_3]$$
7

The attachment of two L·Cu units to the $Pt(CN)_4$ center occurred in the trans fashion in all three cases, yielding the trinuclear complexes **8**, **9** and **10**. As expected, these complexes have a higher thermal stability than their nickel-containing analogues **2**, **3** and **4**. Attempts to attach three L·Cu fragments to $[Pt(CN)_4]^{2-}$ failed, despite the fact that such complexes with Cp(dppe)Fe and $Cp(PPh_3)_2Ru$ fragments are known.[16] In the case of (tpa)Cu, however, four such units could again be attached, resulting in pentanuclear **11**. As in the nickel case, all these compounds are blue, and despite their high perchlorate content, specifically in **6** and **11**, none of the compounds was found to be explosive.

trans-$[L{\cdot}Cu\text{-}NC\text{-}Pt(CN)_2\text{-}CN\text{-}Cu{\cdot}L](ClO_4)_2$
8: L = tren; **9**: L = Me_6tren; **10**: L = tpa

$[Pt\{CN\text{-}Cu(tpa)\}_4](ClO_4)_6$
11

Structure Determinations

Dinuclear Complexes

The structure of the dinuclear cation of **1** is shown in Figure 1. The asymmetric unit of the orthorhombic crystals contains two independent half-molecules, each of which is related to the other half by a twofold rotation. This makes C and N of the bridging cyanide indistinguishable and a discussion of the bond lengths for the bridging ligand irrelevant. Yet these bond lengths are close to those in the related complexes with Me_3tren and Me_6tren ligands.[14,15] The most notable feature in the structure of **1** is the bending of the Cu-C-N (or Cu-N-C) arrays, which is moderate yet significant, with angles of 164.7(3) and 170.2(3)°.

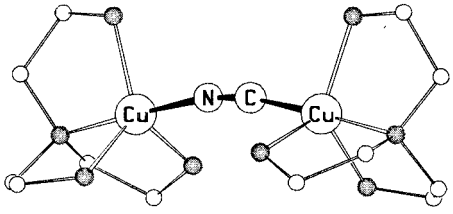

Figure 1. Structure of one of the two independent dinuclear cations of complex **1**; relevant bond lengths: Cu−C or Cu−N 2.008(9) or 1.956(9); C−N 1.134(18) or 1.138(18) Å

The neutral complex **7** also has two formula units in the asymmetric unit and shares the low crystal quality, which is obvious from the high *R* value, and an irregular spread of Pt−C, C−N and Cu−N bond lengths. Thus the structure is mainly a proof of the identity of the complex (Figure 2). Again, there is a slight bending along the Pt-C-N-Cu sequence with Pt−C−N angles of 174(2)° and Cu−N−C angles of 169(2)°. Again there is a closely related and structurally similar reference compound: $[(NH_4)_3Cu\text{-}NC\text{-}Pt(CN)_3]$.[17]

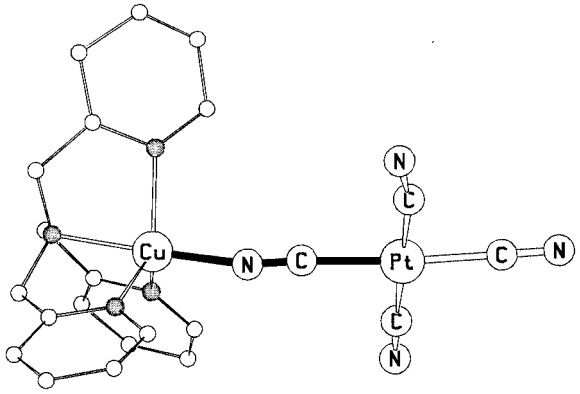

Figure 2. Structure of one of the two independent complex molecules of **7**; relevant bond lengths: Pt−C 1.91(2) and 2.02(2); Cu−N 1.95(2) and 1.94(2); C−N 1.19(3) and 1.09(3) Å.

Trinuclear Complexes

According to our experience the attachment of two ML_n units to $[Ni(CN)_4]^{2-}$ or $[Pt(CN)_4]^{2-}$ leads to trans arrays for steric reasons.[2,16] The *cis*-trinuclear complex **5** is a singular exception to this rule. The complex cation (Figure 3) has twofold symmetry. It is noteworthy that the Ni−C as well as the C−N bond lengths are identical for the terminal and the bridging cyanides. In this complex the bending of the Ni-C-N-Cu array is a means of identifying the C and N atoms of the bridging cyanide: characteristically[1−6] the Ni−C−N angle is close to 180° while the Cu−N−C angle (169°) deviates noticeably from linearity.

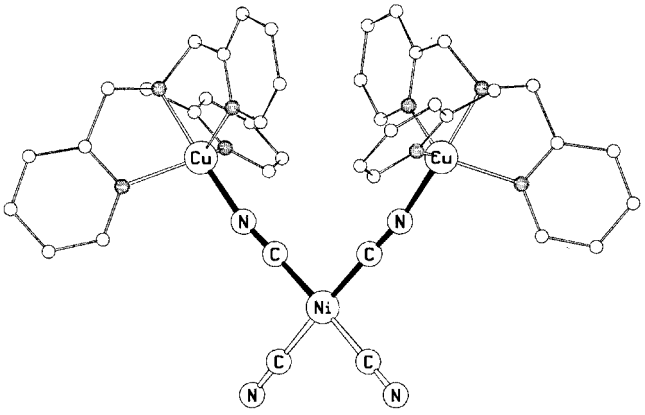

Figure 3. Structure of the trinuclear cation of **5**; relevant bond lengths (Å) and angles (°): Ni−C(term) 1.845(2), Ni−C(br) 1.842(2), C−N(term) 1.163(7), C−N(br) 1.161(7), Cu−N 1.938(5), Ni−C−N(br) 177.5(7), Cu−N−C 168.9(5)

The two $PtCu_2$ complexes **8** and **10** (Figure 4 and 5) can be discussed together. Both contain the Pt center in a virtually ideal square-planar environment, both have the platinum atom on a center of symmetry, both have nearly linear Pt−C−N(bridge) arrays, and in both cases the Cu-N-C array is significantly bent. Again the Pt−C distances are the same for the terminal and the bridging cyanides which seems to indicate that the L·Cu units have rather low σ-acceptor properties. This is reflected by the identical C−N bond lengths for the terminal and bridging cyanides in **10**. These bond lengths differ by 0.08 Å in **8**, which however, like in **7**, may be a reflection of low crystal quality. Most of these features correspond to those of the *trans*-$Pt(CN)_4$ complex with terminal FeCp(dppe) units.[2]

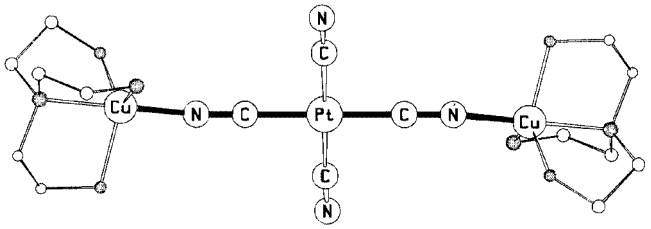

Figure 4. Structure of the trinuclear cation of **8**; relevant bond lengths (Å) and angles (°): Pt−C(term) 1.96(1), Pt−C(br) 1.96(1), C−N(term) 1.12(2), C−N(br) 1.20(2), Cu−N 1.92(1); Pt−C−N(br) 179(1), Cu−N−C 169(1)

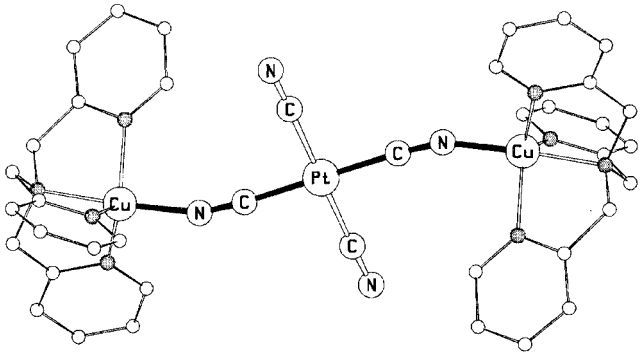

Figure 5. Structure of the trinuclear cation of **10**; relevant bond lengths (Å) and angles (°): Pt−C(term) 1.987(7), Pt−C(br) 1.988(6), C−N(term) 1.142(8), C−N(br) 1.146(8), Cu−N 1.953(5); Pt−C−N(br) 176.0(6), Cu−N−C 160.0(5)

Pentanuclear Complexes

Complexes **6** (Figure 6) and **11** (Figure 7) seem to be the first derivatives of $[Ni(CN)_4]^{2-}$ and $[Pt(CN)_4]^{2-}$ in which all four cyanide ligands are bridging. There are, however, numerous star-like complexes of the type $M(\mu\text{-}CN\text{-}M'L_n)_x$,[7] and the closest relative of **6** and **11** is $[Fe\{CN\text{-}Cu(tpa)\}_6]^{8+}$.[18] While the low crystal quality of **6** renders its structure determination only useful as a product identification, the good crystal quality of **11** allows a meaningful discussion of its molecular dimensions. Complexes **6** and **11** are not isostructural, and only in **6** is the central metal on a center of symmetry. Nevertheless the general appearance of both complexes is quite similar: there is only a small spread of the Ni−C, Pt−C, C−N and Cu−N bond lengths, and these bond lengths correspond closely to those in the trinuclear complexes. There is, however, a variable degree of bending in the Cu-N-C-M-C-N-Cu chains. In **6** one of these chains is linear to a good approximation, the other shows severe bending in a wave-like fashion, as expressed by the

Cu−N−C angle of 162°. In **11** the Cu−N−C angles vary progressively from 176 to 165°, the Pt−C2−N2−Cu2 array is closest to linearity and the Pt−C1−N1−Cu1 array is most distorted.

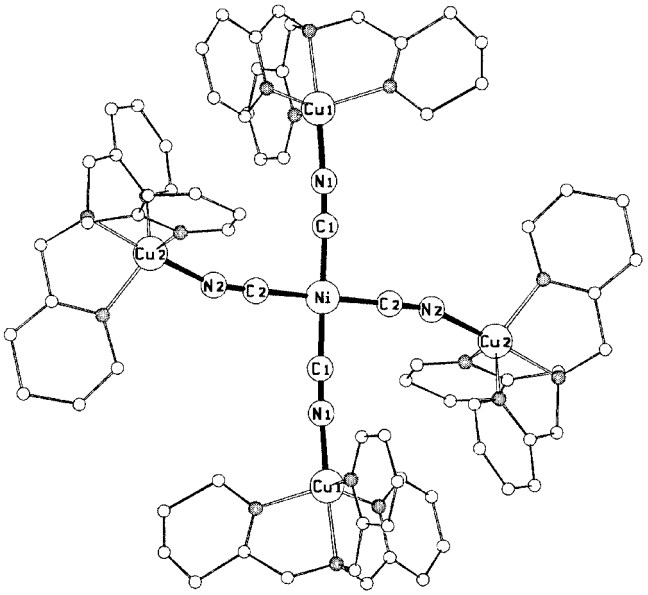

Figure 6. Structure of the pentanuclear cation of **6**; relevant bond lengths (Å) and angles (°): Ni−C1 1.84(2), Ni−C2 1.86(2), C1−N1 1.16(2), C2−N2 1.16(2), Cu1−N1 1.92(2), Cu2−N2 1.94(2); Ni−C1−N1 176.7(14), Ni−C2−N2 178.0(15), Cu1−N1−C1 176.0(18), Cu2−N2−C2 161.9(17)

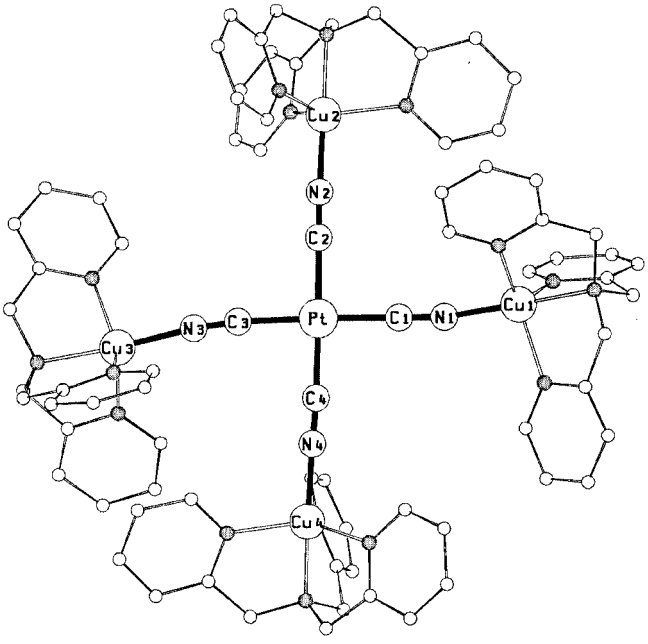

Figure 7. Structure of the pentanuclear cation of **11**; relevant bond lengths (Å) and angles (°): Pt−C1 2.004(6), Pt−C2 1.997(7), Pt−C3 1.995(7), Pt−C4 1.970(7), C1−N1 1.121(8), C2−N2 1.135(8), C3−N3 1.112(8), C4−N4 1.139(8), Cu1−N1 1.940(6), Cu2−N2 1.935(6), Cu3−N3 1.949(6), Cu4−N4 1.948(6); Pt−C1−N1 179.4(7), Pt−C2−N2 179.0(6), Pt−C3−N3 174.0(6), Pt−C4−N4 176.0(7), Cu1−N1−C1 165.2(6), Cu2−N2−C2 176.2(6), Cu3−N3−C3 173.8(6), Cu4−N4−C4 170.4(7)

Altogether it must be stated that the structures of these copper-containing complexes yield only few data for comparative discussions, unlike those of the organometallic complexes that we investigated previously.[1−6] None of the pertinent bond lengths Pt−C, Ni−C, C−N or Cu−N varies significantly with the number of bridging cyanides or the geometry of the complexes. This seems to indicate that the copper(II) ion in those compounds is neither a good π-donor nor a strong σ-acceptor. Thus the Ni−C and Pt−C π-backbonding, which is reflected in the Ni−C, Pt−C and C−N bond lengths, does not vary much, accounting for the similar features of all complexes which were structurally characterized here.

IR Spectroscopy

IR spectroscopy is a more sensitive probe than structure determination for bonding variations in M-CN-M′ arrays. Previously we had observed for $L_2Pt(\text{-CN-M}')_2$ systems with organometallic building blocks M′ that the increase of $\tilde{\nu}$(CN) upon coordination of the second metal (which is a general phenomenon due to the kinematic effect) is modulated in a typical way by the π-donor and σ-acceptor properties of the attached metals.[1,2] As a rule the electron withdrawal by the σ-acceptor at the CN's N terminus is compensated by an increased π-donation from the metal at the C terminus, resulting in a reduction in the increase in $\tilde{\nu}$(CN).[2] Table 1 shows that similar effects are also observed here.

Table 1. IR data for the tri- and pentanuclear complexes [in KBr; $\tilde{\nu}$(CN) in cm^{-1}]

Complex	Backbone	CN_{bridge}	$CN_{term.}$
$[Ni(CN)_4]^{2-}$			2112
$[Pt(CN)_4]^{2-}$			2123
2	*trans*-$Ni(CN\text{-}Cu)_2$	2176	2125
3	*trans*-$Ni(CN\text{-}Cu)_2$	2172	2135
4	*trans*-$Ni(CN\text{-}Cu)_2$	2159	2126
5	*cis*-$Ni(CN\text{-}Cu)_2$	2158	2137, 2126
6	$Ni(CN\text{-}Cu)_4$	2175	
8	*trans*-$Pt(CN\text{-}Cu)_2$	2165	2139
9	*trans*-$Pt(CN\text{-}Cu)_2$	2182	2147
10	*trans*-$Pt(CN\text{-}Cu)_2$	2169	2137
11	$Pt(CN\text{-}Cu)_4$	2196	

For all tri- and pentanuclear complexes the IR bands of the terminal and bridging CN ligands can be clearly discerned. The band positions for the terminal cyanides are only slightly different from those of the $[M(CN)_4]^{2-}$ complexes. In contrast, $\tilde{\nu}$(CN) for the bridging cyanides rises considerably, in fact much more than for the analogous complexes with external organometallic building blocks.[2,16] The number of the CN absorptions corresponds to the symmetry of the complexes. This is also the basis for the assignment of the *trans*-symmetry for **4**, while the *cis*-symmetry of its isomer **5**, which was confirmed by the structure determination, is also reflected in the higher number of its $\tilde{\nu}$(CN) IR bands.

The $\tilde{\nu}$(CN) values due to the CN bridges can be interpreted satisfactorily by a variable degree of π back-donation from the Ni and Pt centers. Compared to the $[M(CN)_4]^{2-}$ references the values are raised by 42−64 cm^{-1} for the trinuclear and by 63 and 73 cm^{-1} for the pentanuclear complexes. In the pentanuclear complexes the π-backbonding capacity of the central metals has to be shared by four CN ligands and hence their $\tilde{\nu}$(CN) values are lowered to a lesser degree than those of the trinuclear complexes (after the raising due to the kinematic effect). Among the trinuclear complexes those with the Cu(tpa) units have (on average) the lowest $\tilde{\nu}$(CN) values. This sheds light on the origin of the variable π-backdonation: the aromatic tripod tpa provides less electron density to the copper ions than the aliphatic tripods tren and Me_6tren. Hence the Cu(tpa) unit is a better σ-acceptor, which in turn forces the central metal to provide more π back-donation. As mentioned above, these effects are smaller here than for the analogous complexes with organometallic constituents.[2,16] Yet, unlike the data from the structure determinations, they have yielded a consistent interpretation of the electronic situation of the various M-CN-Cu groupings.

Electronic Spectra

Cu^{II} in a trigonal-bipyramidal ligand environment gives rise to two d-d transitions in the visible or NIR range which are the origin of its bluish colours.[19] In practice one broad band at 700−800 nm with a more or less pronounced shoulder on the higher energy side is observed.[20] This is also the case here. Table 2 lists the data for the main absorption bands.

Table 2. Electronic spectra (solvent acetonitrile, λ in nm, ε in $M^{-1}\cdot cm^{-1}$)

Complex	Backbone	$\lambda_{max}(\varepsilon)$
tren complexes		
$[Cu(tren)H_2O](ClO_4)_2$		870(140)
2	*trans*-Ni(CN-Cu)$_2$	815(315)
8	*trans*-Pt(CN-Cu)$_2$	835(315)
Me_6tren complexes		
$[Cu(Me_6tren)H_2O](ClO_4)_2$		850(500)
3	*trans*-Ni(CN-Cu)$_2$	805(1400)
9	*trans*-Pt(CN-Cu)$_2$	830(1100)
tpa complexes		
$[Cu(tpa)CH_3CN](ClO_4)_2$		860(150)
4	*trans*-Ni(CN-Cu)$_2$	755(550)
5	*cis*-Ni(CN-Cu)$_2$	745(670)
10	*trans*-Pt(CN-Cu)$_2$	840(2100)
6 Ni(CN-Cu)$_4$		760(1100)
11 Pt(CN-Cu)$_4$		840(2100)

Three features are noticeable. First, all absorptions for the cyanide-bridged complexes occur at higher energies than those for the cyanide-free L·Cu-X reference compounds. Second, nickel induces a much stronger band shift than platinum. Third, the band positions are independent of the number of L·Cu units attached to the $M(CN)_4$ center. A detailed discussion of these phenomena would require quantum mechanical calculations. Qualitatively, it can be stated, however, that the cyanide ligand, even in its isocyanide orientation, exerts a moderately strong ligand field to the L·Cu unit and that this ligand field is modulated strongly by the central metal. In terms of long-range metal-metal interactions there seems to be no effect, since only the type of connectivity (e.g. Ni-CN-Cu) but not the number of such connectivities determines the energy of the electronic transition.

Considering the fact that the Cu/Pt complexes contain Pt^{II} as a reducing and Cu^{II} as an oxidizing metal, one might envisage the occurrence of a Pt^{II} to Cu^{II} MMCT absorption. Actually the reverse charge transfer, with Pt^{IV} as acceptor, has been observed in related Fe/Pt complexes.[21] However, in the measurement window from 300 to 2500 nm no feature indicative of such a MMCT could be observed.

Electrochemistry

Cyclic voltammetry is the best method for evaluating remote metal-metal interactions in ligand-bridged systems. It has allowed us to show for the first time that there is directionality in such interactions, i.e. in $L_2Pt(CN\text{-}M')$ systems they occur for the linear [*trans*-$Pt(CN)_2$], but not for the bent [*cis*-$Pt(CN)_2$] array.[2] This was one of the reasons for the present study: it could be expected that the inert $[M(CN)_4]^{2-}$ centers would ensure electrochemical stability for their oligonuclear derivatives, and one could hope to obtain isomeric cis and trans complexes. Both expectations were fulfilled, albeit only partially. Table 3 lists the electrochemical data that were obtained.

Table 3. Electrochemical data for the Cu(tpa) complexes (in CH_3CN, scan rate 100 mV/s, potentials vs. Ag/AgCl)

Complex	Backbone	$E_{1/2}$ (red)
$[Cu(tpa)CH_3CN](ClO_4)_2$		−0.05 (rev.)
4	*trans*-Ni(CN-Cu)$_2$	−0.30 (irrev.)
5	*cis*-Ni(CN-Cu)$_2$	−0.24 (irrev.)
10	*trans*-Pt(CN-Cu)$_2$	−0.13, −0.26 (rev.)
6 Ni(CN-Cu)$_4$		−0.10, −0.33 (quasirev.)
11 Pt(CN-Cu)$_4$		−0.10, −0.29 (rev.)

It turned out that the tren and Me_6tren complexes decomposed during the cyclovoltammetric experiments. The tpa complexes yielded satisfying cyclic voltammograms, the most informative of which is shown in Figure 8. All oligonuclear complexes are more difficult to reduce than the mononuclear reference compound, corresponding to the fact that the cyanometalate "ligand" $[M(CN)_4]^{2-}$ increases the electron density at copper. Likewise, the nickel-containing complexes are more difficult to reduce than the platinum-containing ones, which may reflect the different electron-releasing properties of these two metals. Although one might want to discuss cis-trans effects for the two isomeric

nickel complexes **4** and **5**, the irreversible nature of their redox processes prevents this.

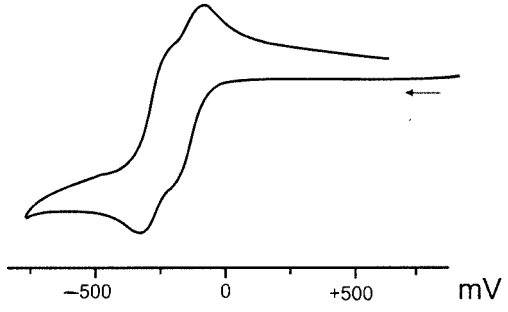

Figure 8. Cyclic voltammogram of complex **10** (in CH_3CN, scan rate 100 mV/s, potentials vs. Ag/AgCl)

The most important observation from the electrochemical measurements is the splitting of the redox wave of the *trans*-Pt(CN-Cu)$_2$ complex **10**. This is proof of the long-range interaction between the two copper ions across two cyanide bridges over a distance of about 10 Å. The number of proven such interactions is still quite small, as they require a redox-inert central metal.[1−12] So far we have observed this interaction only for *trans*-configured trinuclear complexes with central L_2Pt,[2] (Pc)Fe[4] and (salen)M units [M = Cr^{III} or Co^{III}].[6] Like **10**, the pentanuclear complexes **6** and **11** show two redox steps in the reduction of their four Cu(tpa) units. Their separation is larger than the typical one for M′-NC-M-CN-M′ systems (0.05−0.15 V), and the two steps must each represent two-electron reductions. We propose that this again reflects remote metal-metal interactions, both along the two linear Cu-NC-M-CN-Cu arrays, and that the larger potential separation reflects the fact that two electrons are already injected in the first redox step. However, it cannot be excluded that in the first step both copper ions of one linear Cu-NC-M-CN-Cu array are reduced and then the remaining two.

The splitting of the redox waves for **6**, **10** and **11** raised hopes that mixed-valent species might be obtained by partial reduction of the complexes, which might then be investigated for long-range MMCT by UV/Vis-NIR spectroscopy. So far, however, our attempts to achieve this have been unsuccessful.

Conclusions

This work has again shown that square-planar tetracyanometalates are good building blocks for oligonuclear cyanide-bridged complexes that show long-range metal-metal interactions. Between one and four external L·Cu units could be attached to the Ni(CN)$_4$ and Pt(CN)$_4$ centers, and the resulting star-like M(CN-Cu)$_4$ complexes are the first of their kind. The structure determinations have shown that the Cu-NC-M-CN-Cu arrays have a good degree of linearity, but in some cases are noticeably bent at the nitrogen atoms.

The IR absorptions of the C≡N vibrations have allowed some conclusions to be drawn on the electronic situation of the M-CN-Cu arrays. The L·Cu units seem to be both weaker σ-acceptors and π-donors than the organometallic units investigated previously. As a result the kinematic effect is the dominating one in determining the $\tilde{\nu}$(CN) values, and π-backbonding from platinum or nickel to the CN ligands is small, with the effect that the CN IR bands occur at rather high energies.

The electrochemical measurements have again proved the presence of remote metal-metal interactions due to the fact that the complexes containing Cu(tpa) units yield useful cyclic voltammograms. As observed previously, the light central metal (Ni) does not allow the detection of long-range Cu−Cu interactions by means of a splitting of the Cu^{II}/Cu^{I} redox waves. With platinum at the center, however, this splitting occurs. Its order of magnitude corresponds to that previously observed for trinuclear complexes with external organometallic units, thereby supporting the reasonable notion that it is the central and not the external metal unit which controls the long-range metal-metal interactions.

Experimental Section

General: The general working and measuring procedures and the syntheses of the cyanometalates are listed in refs.[1,2] The copper reagents [Cu(tren)H_2O](ClO$_4$)$_2$ (**A**),[22] [Cu(Me$_6$tren)H_2O](ClO$_4$)$_2$ (**B**)[22] and [Cu(tpa)CH_3CN](ClO$_4$)$_2$ (**C**)[23] were prepared as described.

1: A solution of complex **A** (140 mg, 0.33 mmol) in 20 mL of dimethylformamide was added droppwise with stirring into a solution of (PPN)$_2$[Ni(CN)$_4$] (100 mg, 0.08 mmol) in 20 mL of dimethylformamide. The mixture was stirred for 2 h, evaporated to 10 mL and layered with diethyl ether. After one week 45 mg (68%) of **1** had separated as blue crystals, m.p. 180 °C (dec.). $C_{13}H_{36}Cl_3Cu_2N_9O_{12}$·DMF (743.93 + 73.10): calcd. C 23.52, H 5.30, N 17.14; found C 23.48, H 5.28, N 17.18.

2: A solution of complex **A** (96 mg, 0.23 mmol) in 20 mL of methanol was added dropwise with stirring into (140 mg, 0.11 mmol) of (PPN)$_2$[Ni(CN)$_4$] in 20 mL of methanol, upon which a blue precipitate was formed. After 2 h the precipitate was filtered off and washed with dichloromethane and then dissolved in a minimum amount of dimethylformamide. Layering with diethyl ether yielded, within one week, 53 mg (60%) of **2** as a blue powder, m.p. 190 °C (dec.) (the crystalline raw product lost its solvent of crystallization upon drying). $C_{16}H_{36}Cl_2CuN_{12}NiO_8$ (781.23): calcd. C 24.59, H 4.64, N 21.52; found C 24.51, H 4.40, N 21.29.

3: A solution of complex **B** (100 mg, 0.194 mmol) in 20 mL of acetonitrile was added dropwise with stirring to a solution of (PPN)$_2$[Ni(CN)$_4$] (120 mg, 0.97 mmol) in 20 mL of acetonitrile. After 10 h of stirring the solvent was removed in vacuo and the residue washed with dichloromethane. Workup as before for **2** yielded 15 mg (15%) of **3** as a blue powder, m.p. 175 °C (dec.). $C_{28}H_{60}Cl_2Cu_2N_{12}NiO_8$·DMF (949.33 + 73.10): calcd. C 36.41, H 6.60, N 17.80; found C 36.33, H 6.84, N 16.49.

4: A solution of complex **C** (96 mg, 0.16 mmol) in 30 mL of methanol was added dropwise with stirring to a solution of (PPN)$_2$[Ni(CN)$_4$] (100 mg, 0.08 mmol) in 20 mL of methanol at 0

°C. After 2 h of stirring the resulting precipitate was filtered off and dried in vacuo. Dissolving in acetonitrile and layering with diethyl ether yielded, within one week, 30 mg (35%) of **4** as blue crystals, m.p. 215 °C (dec.). $C_{40}H_{36}Cl_2Cu_2N_{12}NiO_8$ (1069.49): calcd. C 44.92, H 3.39, N 15.71; found C 45.10, H 3.14, N 15.71.

5: A solution of complex **C** (255 mg, 0.43 mmol) in 50 mL of methanol was added dropwise slowly with stirring to a solution of $K_2[Ni(CN)_4]$ (104 mg, 0.43 mmol) in 40 mL of water/methanol (1:1). After 2 h of stirring at 0 °C and subsequent filtration the filtrate was evaporated to dryness. The residue was dissolved in acetonitrile, filtered and the solvents evaporated to dryness again. Dissolving the residue in a minimum amount of acetonitrile and layering with diethyl ether produced, within one week, a mixture of blue-green and colourless crystals. The blue-green crystals were separated manually, and recrystallized again from acetonitrile layered with diethyl ether, resulting in 20 mg (4%) of **5** as blue-green crystals, m.p. 230 °C (dec.). $C_{40}H_{36}Cl_2Cu_2N_{12}NiO_8$ (1069.49): calcd. C 44.92, H 3.39, N 15.71; found C 44.25, H 3.85, N 15.38.

6: Like **4** from $(PPN)_2[Ni(CN)_4]$ (30 mg, 0.24 mmol) and **C** (57 mg, 0.96 mmol). Yield 32 mg (61%) of **6** as blue crystals, m.p. 255 °C (dec.). $C_{76}H_{72}Cl_6Cu_4N_{20}NiO_{24}$ (2175.12): calcd. C 41.97, H 3.34, N 12.88; found C 41.85, H 3.18, N 12.44.

7: A solution of complex **C** (22 mg, 0.04 mmol) in 10 mL of methanol was added dropwise with stirring to a solution of $(PPN)_2[Pt(CN)_4]$ (51 mg, 0.04 mmol) in 10 mL of dichloromethane. After 12 h of stirring the solvent was removed in vacuo, the residue washed with dichloromethane and dried in vacuo. Dissolving in a minimum amount of acetonitrile and layering with diethyl ether yielded, within one week, 9 mg (37%) of **7** as blue crystals, m.p. 204 °C. $C_{22}H_{18}CuN_8Pt$ (653.06): calcd. C 40.46, H 2.78, N 17.16; found C 39.15, H 2.45, N 16.78.

8: A solution of complex **A** (143 mg, 0.34 mmol) in 20 mL of methanol was added dropwise with stirring to a solution of $(PPN)_2[Pt(CN)_4]$ (213 mg, 0.17 mmol) in 20 mL of methanol. After 2 h of stirring the resulting precipitate was filtered off, washed with dichloromethane and dissolved in 5 mL of dimethylformamide, which was layered with diethyl ether. After one week **8** had separated as blue crystals, which crumbled upon drying in vacuo. 100 mg (66%) of solvent-free **8** remained as a blue powder, m.p. 190 °C (dec.). $C_{16}H_{36}Cl_2Cu_2N_{12}O_8Pt$ (917.70): calcd. C 20.94, H 3.95, N 18.32; found C 20.70, H 3.81, N 17.92.

9: Like **3** from **B** (237 mg, 0.45 mmol) and $(PPN)_2[Pt(CN)_4]$ (294 mg, 0.21 mmol). Yield 45 mg (18%) of **9** as a blue powder, m.p. 180 °C (dec.). $C_{28}H_{60}Cl_2Cu_2N_{12}O_8Pt{\cdot}DMF$ (1085.93 + 73.10): calcd. C 32.13, H 5.83, N 15.71; found C 32.41, H 5.73, N 14.47.

10: Like **4** from **C** (129 mg, 0.22 mmol) and $(PPN)_2[Pt(CN)_4]$ (150 mg, 0.11 mmol). Yield 75 mg (57%) of **10** as blue crystals, m.p. 275 °C. $C_{40}H_{36}Cl_2Cu_2N_{12}O_8Pt$ (1205.88): calcd. C 39.84, H 3.01, N 13.94; found C 39.83, H 2.99, N 13.87.

11: Like **4** from **C** (97 mg, 0.16 mmol) and $(PPN)_2[Pt(CN)_4]$ (54 mg, 0.04 mmol). Yield 62 mg (64%) of **11** as blue crystals, m.p. 200 °C (dec.). $C_{76}H_{72}Cl_6Cu_4N_{20}O_{24}Pt{\cdot}2CH_3CN$ (2311.51 + 82.10): calcd. C 40.14, H 3.25, N 12.87; found C 40.05, H 3.13, N 12.85.

Structure Determinations:[24] Crystals were obtained from the reaction mixtures. Diffraction data were recorded at room temp. with a Bruker Smart CCD diffractometer fitted with a molybdenum tube (Mo-K_α, λ = 0.7107 Å) and a graphite monochromator and subjected to empirical absorption corrections. The structures were solved by direct methods and refined anisotropically with the SHELX program suite.[25] Hydrogen atoms were included with fixed distances and isotropic temperature factors 1.5-times those of

Table 4. Crystallographic data

	1	**5**	**6**	**7**	**8**	**10**	**11**
Empirical formula	$C_{13}H_{36}Cl_3Cu_2N_9O_{12}{\cdot}$ DMF	$C_{40}H_{36}Cl_2Cu_2N_{12}NiO_8{\cdot}2CH_3CN$	$C_{76}H_{72}Cl_6Cu_4N_{20}NiO_{24}$	$C_{22}H_{18}CuN_8Pt{\cdot}CH_3CN$	$C_{16}H_{36}Cl_2Cu_2N_{12}O_8Pt{\cdot}6DMF$	$C_{40}H_{36}Cl_2Cu_2N_{12}O_8Pt$	$C_{76}H_{72}Cl_6Cu_4N_{20}O_{24}Pt{\cdot}3CH_3CN$
Molecular mass	743.93 + 73.10	1069.49 + 82.10	2175.12	653.06 + 41.05	917.70 + 438.60	1205.88	2311.51 + 123.15
Crystal size [mm]	0.3 × 0.25 × 0.15	0.4 × 0.2 × 0.1	0.25 × 0.2 × 0.15	0.4 × 0.15 × 0.1	0.8 × 0.6 × 0.5	0.2 × 0.15 × 0.1	0.55 × 0.35 × 0.2
Space group	Pbcn	*C*2/*c*	*C*2/*c*	$P2_1$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
Z	8	4	4	4	4	2	2
a (Å)	11.676(2)	13.010(3)	30.537(3)	9.610(3)	13.012(3)	17.053(13)	11.921(2)
b (Å)	49.142(10)	18.157(4)	17.586(1)	13.381(4)	14.811(3)	9.649(8)	16.979(3)
c (Å)	11.616(2)	21.520(5)	19.568(2)	19.820(5)	15.022(3)	14.511(11)	26.199(4)
α (°)	90	90	90	90	90	90	96.442(3)
β (°)	90	105.056(4)	93.505(2)	92.277(6)	96.88(3)	110.97(2)	100.529(3)
γ (°)	90	90	90	90	90	90	103.784(3)
V (Å^3)	6665(2)	4909(2)	10489(2)	2547(1)	2874(1)	2229(3)	4995(1)
D(calc) (gcm^{-3})	1.62	1.56	1.38	1.81	1.57	1.80	1.62
μ(Mo-K_α) (mm^{-1})	1.59	1.41	1.20	6.35	3.32	4.26	2.48
hkl range	*h:* −13 to 13 *k:* −58 to 58 *l:* −2 to 13	*h:* −17 to 17 *k:* −24 to 24 *l:* −28 to 28	*h:* −33 to 33 *k:* −19 to 19 *l:* −21 to 21	*h:* −6 to 12 *k:* −17 to 14 *l:* −21 to 22	*h:* −14 to 14 *k:* −16 to 0 *l:* −17 to 0	*h:* −12 to 17 *k:* −12 to 2 *l:* −19 to 18	*h:* −15 to 15 *k:* −21 to 21 *l:* −34 to 34
Measured reflections	13571	21722	36160	7737	3566	6436	45719
Independent reflections	5879	5871	7562	7473	3460	4257	23379
Observed refl. [$I > 2\sigma(I)$]	3495	2057	4158	4246	3122	3079	14520
Parameters	400	326	592	617	322	295	1264
Refined reflections	5879	5871	7562	7473	3460	4257	23379
R_1 (obs.refl.)	0.096	0.083	0.149	0.089	0.072	0.038	0.053
wR_2 (all refl.)	0.303	0.171	0.433	0.243	0.244	0.104	0.168
Residual electron density (e/Å^3)	+1.5/−0.8	+0.8/−0.9	+2.1/−0.9	+3.3/−3.1	+1.8/−2.1	+1.5/−1.5	+3.1/−1.9

their attached atoms. Parameters were refined against F^2. The R values are defined as $R_1 = \Sigma|F_0 - F_c|/\Sigma F_o$ and $wR_2 = \{\Sigma[w(F_0^2 - F_c^2)^2]\Sigma[w(F_0^2)^2]\}^{1/2}$. Drawings were produced with SCHAKAL.[26] Table 4 lists the crystallographic data.

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