STUDIES OF THE LINKAGE AND BONDING OF TRIATOMICS IN TRANSITION METAL COMPLEXES. PART 2. NCS⁻ COMPLEXES

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ABSTRACT

The geometrics of NCS⁻ coordinated to transition metals range over N- or S-linkage, N- or S-bridge, end-to-end bridge and possibly other arrangements. In the coordination of NCS⁻ to transition metals, various metal-to-ligand angles have also been reported. We examine the linkage and mode of binding of NCS⁻ to $Co(NH_3)_5^{3+}$ and to $Ru(NH_3)_5^{2+}$ by fragment analysis of molecular orbital calculations. Together with our studies of the coordination of other triatomics (N_2O, NCO^- and N_3^-) to $M(NH_3)_5^{n+}$ (M=Co, Ru or Os), our results indicate that for the bonding of N_2O, NCO^- and N_3^- to $M(NH_3)_5^{n+}$, (a) complexes with linearly bonded triatomics (i.e. $\angle MXY = 180°$) are more stable, (b) N-linked complexes are more stable, and (c) the metal–ligand bonds are mainly σ bonds with "electron flow" from ligand to metal. For bonding of SCN^- to $M(NH_3)_5^{n+}$, there are two competing stable structures, which are comparable to experimentally known structures: (a) N-linked $[M(NH_3)_5NCS]^{n+}$ is linearly bonded, mainly through σ bonding, and (b) S-linked $[M(NH_3)_5SCN]^{n+}$ is bonded with a $\angle MSC$ bond angle around 120° through both σ and π bonding.

INTRODUCTION

The thiocyanate anion (SCN⁻) has been found to coordinate to transition metals in different modes [1]; there are plentiful examples of the N- or S-bridged variety, end-to-end bridged, and N- or S-linked complexes. The cyanate anion (OCN⁻) in general coordinates to transition metals through the N atom [1–3] with N-bridged, end-to-end bridged (predominantly N-bonded), and non-bridged N-linked varieties. Even if OCN⁻ has not been as common an ambidentate ligand as SCN⁻, the existence of an O-linked cyanate complex has been an often debated issue for many years [1,2]. Except in the case of interaction with other ligands [1,4], the OCN⁻, SCN⁻ and other triatomic fragments in the transition metal complexes are usually linear, but the angle between the metal and the ligand ($\angle MXY$) depends on several factors [1,5]:

the metal, the triatomic, the packing in the solid state, counter-ions, solvent effects, and possibly steric and trans effects of other ligands.

For SCN^-, Lindquist and Strundberg [6] first observed the general pattern that class b metals form S-linked complexes and class a metals form N-linked complexes. This behavior parallels the division of metal ions [7] (in their common oxidation states) into class a acceptors, which bind most strongly with ligands containing second row elements (O, N, F etc.) as donor atoms, and class b acceptors, which form their most stable complexes with elements in higher periods of the periodic tables (P, S, Cl etc.). Exceptions to this general pattern were found [1] in the cases where a certain metal can form both N-linked and S-linked bonds with SCN^- in one complex or in different complexes, where the SCN^- forms an end-to-end bridge between metal atoms of the same kind, and where there are N- and S-linkage isomerism. Rationalizations have been proposed to explain the modes of coordination of SCN^-, OCN^- and other triatomics to transition metals. Some [8] used the analogy of O in OCN^- and S in SCN^- to support the possibility of O-bonded OCN^- complexes. Numerous statements in the literature and textbooks suggest the "mainly π-backbonding" character in the coordination of triatomics, based on the analogy with the complexes of diatomics (e.g. CO, N_2, NO^+, CN^-).

In order to understand the bonding and linkage of the triatomics in the transition metal complexes, we set out to study the electronic structure of complexes of the ML_nXYZ type. In a previous paper [2] we analyzed the electronic structure of ML_5XYZ, where $M = Co$, Ru or Os, $L = NH_3$, and $XYZ = N_2O$ or NCO^-. In this paper the complexes of $Co(NH_3)_5^{3+}$ or $Ru(NH_3)_5^{2+}$ to NCS^- are studied, particularly with regard to the N- or S-linkage isomers and the variation in $\angle MXY$. Results of the coordination of N_3^- are given in another paper [9]. Studies of the bonding of ML_nXYZ ($n = 3, 4, 5$) in different geometries, with different coordination, and for different electron counts for the metal are under way. Our aim is to investigate features which are unique to the triatomic ligands.

The calculations carried out were of the extended Hückel type [10,11]. Details are given in the Appendix. Our argument is based on the fragment analysis through a formalism [12] which partitions the molecular species into ML_n and XYZ. From the studies for each ML_nXYZ type complex, many of the general principles we draw, based on symmetry, should carry over to where M is any transition metal, L is any σ-donor, and XYZ is any linear triatomic with 16 valence electrons. Other trends based on numerical results of our calculations can be extrapolated to predict bonding of ML_nXYZ in general.

GENERAL FEATURES OF THE INTERACTION

The formation of an ML_5XYZ complex with C_{4v} symmetry from the end-on coordination of a linear triatomic XYZ to a square pyramidal ML_5 fragment,
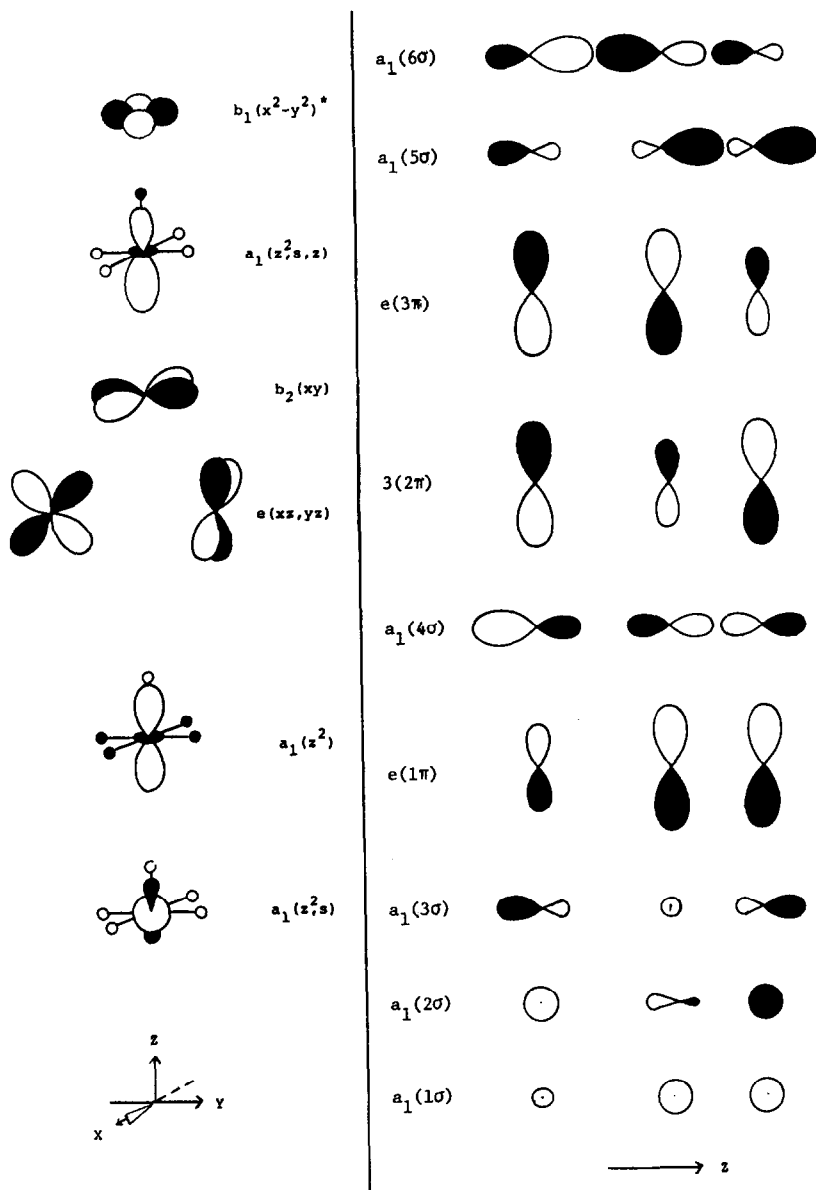
Fig. 1. Schematic drawing of some valence orbitals of a square pyramidal ML_5 (left) and a linear heteronuclear triatomic (right). Orbitals are given in order but not on any energy scale.
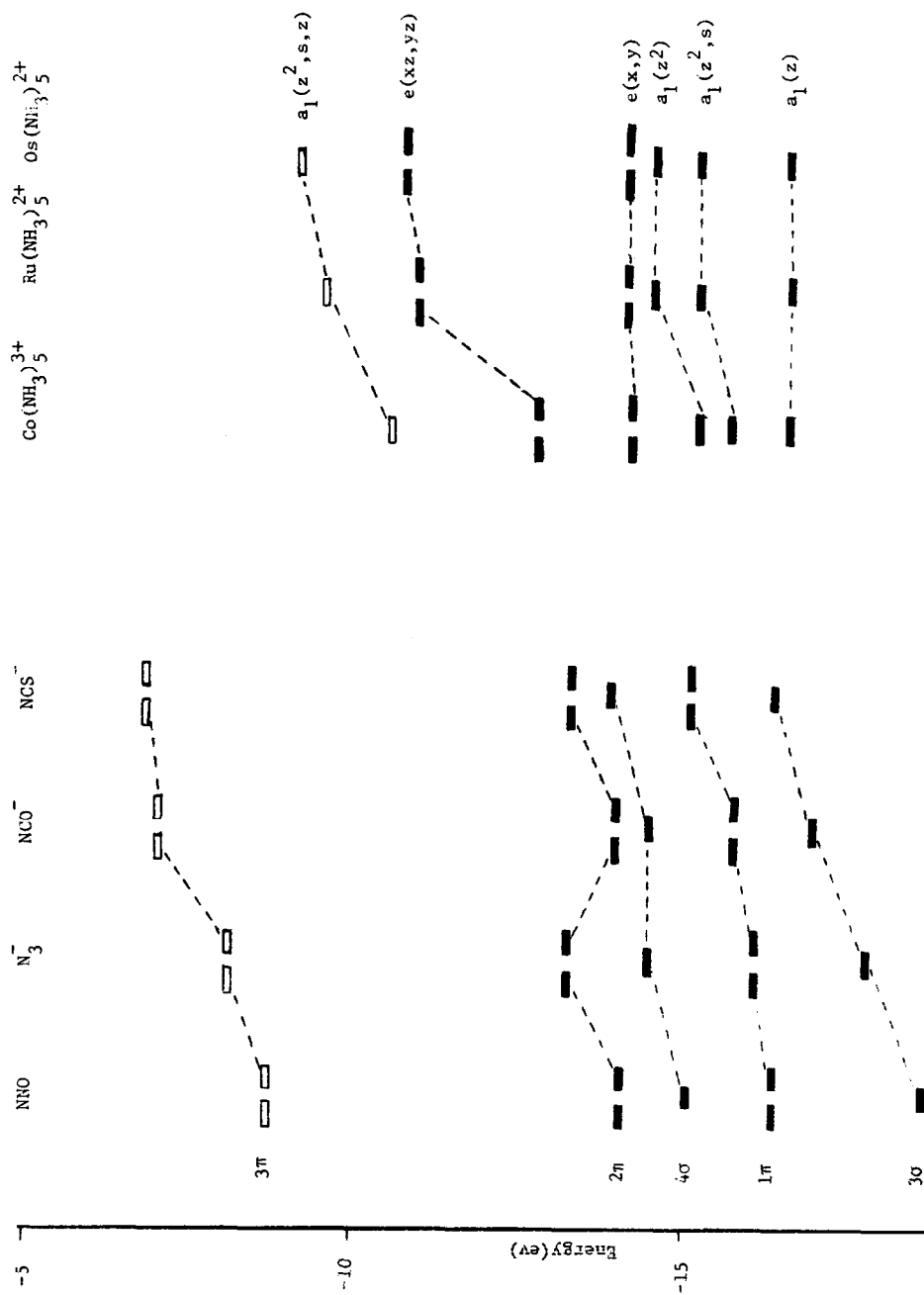
Fig. 2. Valence orbital energies relevant to the symmetry-allowed interaction of different triatomics and $M(NH_3)_5$.
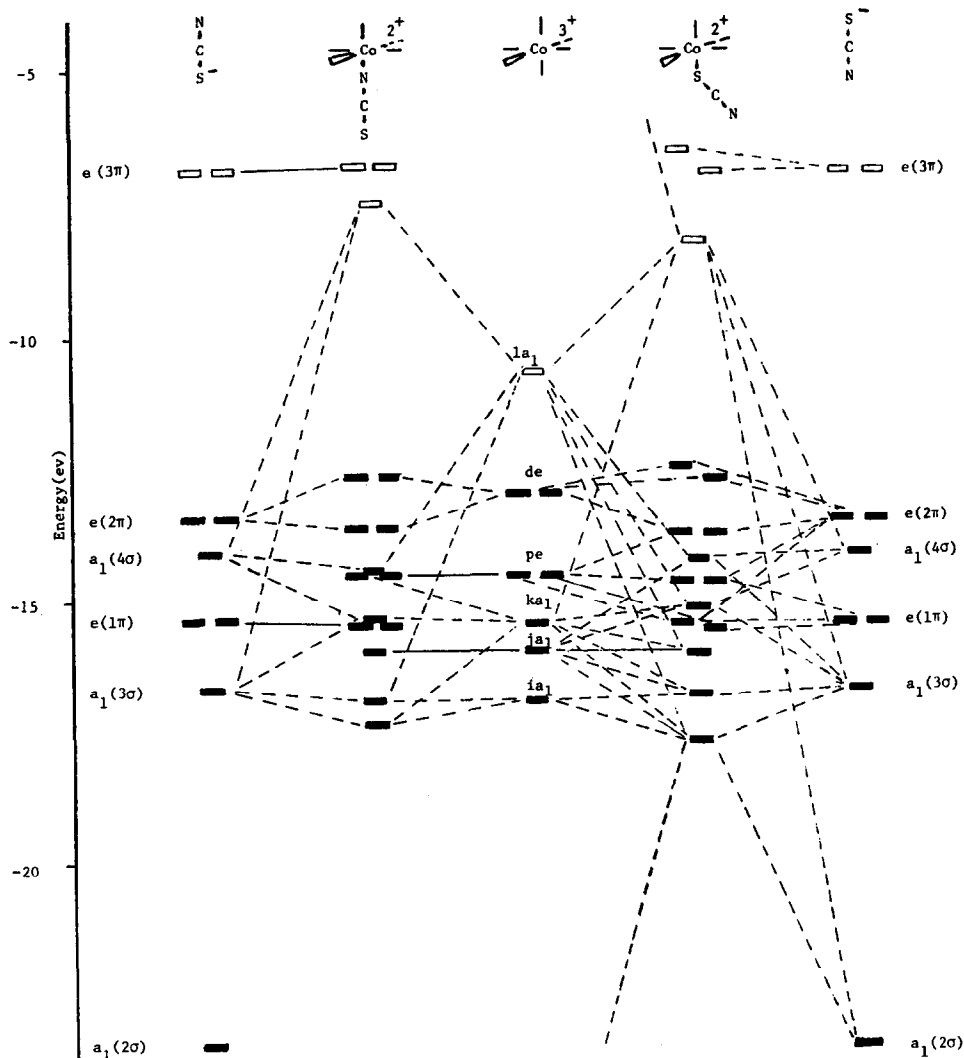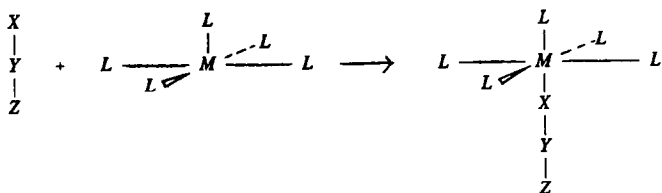
Fig. 3. Interaction diagrams for $Co(NH_3)_5^{3+}$ and NCS^- to form linearly bonded $[Co(NH_3)_5NCS]^{2+}$ (left) and $[Co(NH_3)_5SCN]^{2+}$ with $\angle CoSC$ 120° and dihedral angle 135°.

where the transition metal is in the basal place of the pyramid, is given in Scheme 1. The orbitals of the triatomic [13] and the square pyramidal ML_5 fragment [2,12] are well known. We illustrate some of them schematically in Fig. 1. These are only the valence orbitals of XYZ and some of the valence orbitals of the ML_5, which are relevant to the symmetry-allowed interaction between the fragments. In Fig. 1 we purposely indicate the difference in spatial extensions of the orbitals due to the difference in the three atoms X, Y and Z

in a heteronuclear triatomic. The labels of orbitals of the triatomic are based on $C_{\infty v}$ symmetry in the linear XYZ and on C_{4v} symmetry in the ML$_5$XYZ. The orbitals of ML$_5$ are referred to by their metal d-character and the C_{4v} symmetry of the complex [2].

$$
\begin{array}{ccc}
X \\
| \\
Y \quad + \quad L\!-\!\!-\!\!-\!M\!\!=\!\!\!-\!L \quad \longrightarrow \quad L\!-\!\!-\!\!-\!M\!\!=\!\!\!-\!L \\
| \\
Z
\end{array}
$$

Scheme 1.

The strength of the symmetry-allowed interactions between the fragment orbitals depends on the amount of overlap between the orbitals and the compatibility of the orbital energies. These factors will vary with the metal, triatomic, other ligands and the M–X separation. For the systems we have studied here and elsewhere [2,9], the orbital energies of different XYZ and ML$_5$ relevant to the bonding are given in Fig. 2. Our calculations indicate that the following interactions in the ML$_5$XYZ type complexes are important enough to be investigated.

(a) Among the interaction of e orbitals, based on the compatibility of orbital energies, only the interactions between e(3π) and/or e(2π) of XYZ and e(xz,yz) and e(x,y) of ML$_5$ are significant enough to be considered.

(b) For the interaction of a$_1$ orbitals, according to the degree of the extension of the electron density toward the site below the basal plane (illustrated in Fig. 1), a$_1(z^2,s,z)$ of ML$_5$ is the orbital which strongly interacts with a$_1$ (3σ) and a$_1$ (4σ) of a triatomic approaching this site. The a$_1(z^2)$, a$_1(z^2,s)$ and a$_1(z)$ of ML$_5$ only mix in the resulting orbitals through secondary interactions.

To illustrate the relations between the energies of the fragment orbitals and the composite orbitals, the interaction diagram of Co(NH$_3$)$_5^{3+}$ and SCN$^-$ to form the linearly bonded [Co(NH$_3$)$_5$NCS]$^{2+}$ and "bent-bonded" [Co(NH$_3$)$_5$SCN]$^{2+}$ are given in Fig. 3. In Fig. 3, for the orbitals of Co(NH$_3$)$_5^{3+}$, e(xy,yz), e(x,y) are referred to as de and pe, and we use i, j, k, l to distinguish the a$_1(z)$, a$_1(z^2,s)$, a$_1(z^2)$ and a$_1(z^2,s,z)$ orbitals.

CRITERIA FOR ANALYSIS OF THE LINKAGE AND BONDING BETWEEN M(NH$_3$)$_5$ AND XYZ

In analyzing the bonding of fragments to form the complex, we use three criteria as indicators [2].

Stabilization energy (E$_{st}$)

This is defined as the difference between the sum of the total energy of the fragments, E_{frag}, and the total energy of the composite complex, E_{com}:

$$E_{st} = \sum_{frag} E_{frag} - E_{com}$$

E_{st} can also be separated into stabilization energies due to σ and π bonding, $E_{st,\sigma}$ and $E_{st,\pi}$, which are defined as

$$E_{st,\sigma} = \sum_{frag} \sum_i \epsilon_{i\sigma,frag} - \sum_i \epsilon_{i\sigma,com}$$

$$E_{st,\pi} = \sum_{frag} \sum_i \epsilon_{i\pi,frag} - \sum_i \epsilon_{i\pi,com}$$

where $E_{st} = E_{st,\sigma} + E_{st,\pi}$, and $\epsilon_{i\sigma,frag}$, $\epsilon_{i\pi,frag}$, $\epsilon_{i\sigma,com}$ and $\epsilon_{i\pi,com}$ are the ith σ- and π-orbital energies of the fragments and the complex respectively.

The number of electrons that flow from one fragment to another, #e(donor→acceptor)

The electrons mainly flow from the highest occupied orbitals of the donor fragment to the lowest unoccupied orbitals of the acceptor fragment. This number can also be separated into the number of π electrons flowing from a π-donor fragment, (#πe), and the number of σ electrons flowing from a σ-donor fragment, (#σe).

Reduced overlap population (Op)

Op(M–X) measures the electron density in the M–X bond. It is an indication of the bond order and can also be used to evaluate the strength of the bond.

RESULTS AND DISCUSSION

Some of the results of our calculations are summarized in Table 1. For all the complexes of triatomics we have studied here and elsewhere [2,9], a few trends can be observed.

For bonding of N_2O, NCO^- or N_3^- to $M(NH_3)_5$, the following trends are observed.

(a) Linearly bonded complexes (i.e. $\angle$ MXY = 180°) are more stable.

(b) N-linked complexes are more stable, as seen by comparing the pairs of N- vs. O-linked complexes (from ΔE in Table 1). This is because in the e(2π) or e(3π) and a$_1$(4σ) orbitals of N_2O and NCO^- the spatial extensions of the N side are always larger than those of the O side (illustrated in Fig. 1) owing to the difference in electronegativities of O and N.

(c) The bonding is mainly σ-bonding with larger $E_{st,\sigma}$ and #σe(XYZ→M), but smaller $E_{st,\pi}$ and #πe(M→XYZ), because of the incompatibility of the energies of e(3π) and/or e(2π) of XYZ and e(xz,yz) of $M(NH_3)_5$ (see Figs. 2 and 3).

For bonding of SCN^- to $M(NH_3)_5^{n+}$, we found two competing stable structures: the N- and S-linked isomers. N-linked $[Co(NH_3)_5NCS]^{2+}$ and $[Ru(NH_3)_5NCS]^+$ are linearly bonded mainly through σ bonding. General

TABLE 1

Stabilization energy, electron flow and overlap population

R (M-X) (Å)	Molecular[a,f,g] species	ΔE (eV)[b]	E_{st} (eV)[c]	$E_{st,\pi}$ (eV)[c]	$E_{st,\sigma}$ (eV)[c]	#πe[d] (M→L')	#σe[d] (L'→M)	OP (M-X)[e]
1.94	CoNCS⁻	−0.81	−1.59	−0.35	−1.93	0.04	0.45	0.43
2.272	CoSCN⁻		−0.77	0.63	−1.40	0.02	0.47	0.44
2.272	CoSCN⁻ (∠CoSC=120°)	−0.54	−1.04	−0.02	−1.03	−0.24	0.26	0.44
2.272	CoSCN⁻ (∠CoSC=104.9°)	−0.65	−0.94	−0.08	−0.85	−0.18	0.32	0.43
2.124	RuNCS⁻		−0.96	−0.16	−0.81	0.04	0.24	0.22
2.458	RuSCN⁻	−0.64	−0.32	0.15	−0.47	0.02	0.25	0.25
2.458	RuSCN⁻ (∠RuSC=120°)	−0.42	−0.54	−0.08	−0.46	0.02	0.27	0.26
1.943	Co-NCO⁻	−0.43	−1.56	0.38	−1.94	0.04	0.47	0.42
	Co-OCN⁻		−1.13	0.31	−1.44	0.02	0.34	0.30
1.943	Co-NNO	−0.57	−1.67	0.09	−1.76	0.10	0.43	0.46
	Co-ONN		−1.12	0.28	−1.40	0.02	0.32	0.31
1.84	Ru-NN		−3.88	−1.35	−2.53	0.92	0.43	0.72
1.77	Ru-NO⁺		−6.98	−4.73	−2.25	2.44	0.40	0.90

[a]$Ru = Ru(NH_3)_5^{2+}$; $Co = Co(NH_3)_5^{3+}$.

[b]$\Delta E = E$ (N-bonded isomer) $- E$ (non-N-bonded isomer).

[c]E_{st} = stabilization energy = $[E(M) + E(L')] - E(ML')$; $M = M(NH_3)_5$, $L' = XYZ$; or XY; $E_{st,\pi} = E_{st}$ due to π bonding, and $E_{st,\sigma} = E_{st}$ due to σ bonding.

[d]#πe(M→L') = number of π electrons flowing from $M(NH_3)_5$ to XYZ or XY; #σe(L'→M) = number of σ electrons flowing from XYZ or XY to $M(NH_3)_5$.

[e]OP(M-X) = reduced overlap population between metal and the linked atom X in XYZ or in XY.

[f]∠MXY = 180° unless ∠MXY is specified.

[g]Data on complexes of NCO⁻, N_2O, N_2 and NO⁺ are from ref. 2.

features of the bonding are the same as those of the above-mentioned linearly bonded complexes. S-linked $[Co(NH_3)_5SCN]^{2+}$ and $[Ru(NH_3)_5SCN]^+$ are bonded with ∠MSC around 120°, which is comparable to the experimental value ∠CoSC = 104.9° in $[Co(NH_3)_5SCN]^{2+}$ reported by Snow and Boomsma [14]. They involve σ- and π bonding with both σe and πe flow from SCN⁻ to $M(NH_3)_5$. The energy differences between comparable structures with dihedral angles 180° and 135° (e.g. ∠MXY bent in "eclipsed" and "staggered" conformations) are an order of magnitude too small for us to consider here.

Our results indicate that owing to the longer M-S distance in the S-linked isomer, pure σ-bonding is too weak to form a complex. The bending of the ∠MSC angle introduces some π-orbital interaction, strengthens the M-S bond,

and leads to the stable "bent-bonded" S-linked complex. Various sizes of $\angle$ MSC have been reported for S-linked SCN^- complexes [1]; our studies offer a general explanation of these bond angles based on the electronic structure of the complexes. The small calculated energy difference between the linkage isomers confirms the observed isomerism of $[Co(NH_3)_5SCN]^{2+}$ and $[Co(NH_3)_5NCS]^{2+}$ [14]. It also suggests that the stabilities of the linkage isomers $[Ru(NH_3)_5SCN]^+$ and $[Ru(NH_3)_5NCS]^+$ may be comparable; however, both of them may not be stable. The isomerization between $[Ru(NH_3)_5NCS]^{2+}$ and $[Ru(NH_3)_5SCN]^{2+}$, which have an electron count for Ru different from that for Ru studied here, has been observed from UV and IR spectra [15]. Because of the electron donor character of SCN^- in the bonding we studied here, we expect $[Ru(NH_3)_5NCS]^+$ and $[Ru(NH_3)_5SCN]^+$ to be less stable than their Ru(III) counterparts.

CONCLUSIONS

In summary, our studies of the coordination of NCS^- to ML_5 lead to the following conclusions. On the basis of the compatibility of the energies of the fragment orbitals relevant to the interaction, the bonding is mainly through donation of electrons from NCS^- to the metal. There is almost no backbonding. In the calculated stable structures, the M–N bonds of the linearly bonded N-linked isomers have σ character. The M–S bonds of the "bent-bonded" S-linked isomers have both σ and π character.

ACKNOWLEDGMENTS

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APPENDIX

The $M(NH_3)_5XYZ$ calculations which underlie the arguments used in this paper are of the extended Hückel type [10] with "weighted" H_{ii}s [11]. The atomic basis sets included single Slater-type functions for all orbitals except the metal d-orbitals. The parameters for the elements used are listed in Table A1. These parameters are standard ones taken from earlier work [2,10].

When the triatomic ligands are linearly bound to $M(NH_3)_5$ the geometry of $M(NH_3)_5XYZ$ is chosen to have pseudo-C_{4v} symmetry. In studying the variation of the angle $\angle MXY$ in the bent $M(NH_3)_5XYZ$ complexes, the MXY bond is bent in the "eclipsed" or in the "staggered" conformation (i.e. $\angle MXY$ is bent in a plane which contains an $M(NH_3)_3$ plane or bisects the two perpendicular $M(NH_3)_3$ planes of the square pyramidal $M(NH_3)_5$). The bond lengths and bond angles used are given in Table A2. The bond lengths in the ligands, and the metal-to-NH_3 distances are experimental values. For the M–X distances, experimental values are used whenever they are available.

TABLE A1

Extended Hückel parameters

Orbital		H_{ii} (eV)	Exponents[a]	
			1	2
H	1s	−13.60	1.30	
C	2s	−21.4	1.625	
	2p	−11.4	1.625	
N	2s	−26.00	1.95	
	2p	−13.40	1.95	
O	2s	−32.3	2.275	
	2p	−14.8	2.275	
S	3s	−20.00	1.817	
	3p	−13.30	1.817	
Co	3d	−13.18	5.55 (0.55508)	1.90 (0.64609)
	4s	−9.21	2.00	
	4p	−5.29	2.00	
Ru	4d	−11.12	5.380 (0.53427)	2.30 (0.63676)
	5s	−8.60	2.080	
	5p	−3.59	2.040	

[a]Two Slater exponents are listed for the d orbitals, each followed in parentheses by its coefficient in the double-zeta expansion.

TABLE A2

Bond lengths and bond angles

Molecular species	Bond length (Å)	Bond angle (deg)	References
NH_3	N–H 1.015	∠HNH 107	16
NCS^-	N–C 1.14	C–S 1.64	14
$[Co(NH_3)_5NCS]^{2+}$	Co–N 1.94		14
$[Co(NH_3)_5SCN]^{2+}$	Co–N 1.94	Co–S 2.272	14
$[Ru(NH_3)_5NCS]^+$	Ru–N 2.124		–[a]
$[Ru(NH_3)_5SCN]^+$	Ru–N 2.124	Ru–S 2.458	–[a]

[a]In the SCN^- complexes, bond lengths of Ru–N and Ru–S are scaled from those of Co–N and Co–S (ref. 14) by adding the difference of bond lengths (0.184 Å) of Co–NH_3 and Ru–NH_3 in OCN^- complexes (ref. 2).