the higher entropy. Most exceptions can be explained away by high-spin–low-spin variations, making the intermediate complexes less favored, though, as Kida[7] pointed out, certain facts about cyanides are difficult to understand. The symbiosis is clear in cobalt(III) complexes, where $Co(NH_3)_5X^{2+}$ is far better bound for $X = F$ than I, showing (a) characteristics, whereas $Co(CN)_5X^{3-}$ is most stable with $X = I$ and not even known for $X = F$. The very soft base $H^-$ also forms $Co(CN)_5H^{3-}$. We may remember Pauling's effect that, under equal circumstances, the characteristic coordination number of (b) ligands tends to be lower than of (a) ligands (*cf.* $CoCl_4^{2-}$ and $Co(H_2O)_6^{2+}$). This is not so much a question of larger atomic size as of an appropriate amount of electronic density being donated from a lower number of soft ligands.

The author and his colleague, Dr. H.-H. Schmidtke, attempt now to elucidate the symbiotic tendency by various MO calculations. Since the optical electronegativity[8] of the central atom $nd$ shell increases monotonically with $z$, the empty $(n + 1)s$ orbital may be more important. The nonmonotonic behavior as a function of $z$ might be connected with the empty $(n + 1)s$ orbital producing strong characteristics of a soft acid for low $z$, whereas the somewhat less pronounced (b) properties for very high $z$ are caused by the near coincidence of the energies of a partly filled $nd$ shell with the filled orbitals of the ligands. In the intermediate $z$ range, covalent bonding is less conspicuous because both $(n + 1)s$ and $nd$ have much higher energy than the ligand orbitals.

(7) S. Kida, *Bull. Chem. Soc. Japan*, **34**, 962 (1961).
(8) C. K. Jørgensen, "Orbitals in Atoms and Molecules," Academic Press, London, 1962.

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## Importance of Steric Factors in the Type of Metal–Ligand Bonding, M–SCN or M–NCS, for Analogous Metal Complexes[1]

*Sir:*

It is well known that $SCN^-$ forms both thiocyanato (M–SCN) and isothiocyanato (M–NCS) metal complexes, depending on the metal. Several authors[2] have pointed out that the change from M–NCS to M–SCN bonding coincides approximately, for different metals, to the change in halogenometal complex stabilities from $F^- > Cl^- > Br^- > I^-$ to $I^- > Br^- > Cl^- > F^-$. The first order is followed by class a and the second by class b metals.[3] Several explanations have

(1) Presented at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964.
(2) I. Lindquist and B. Strandberg, *Acta Cryst.*, **10**, 176 (1957); P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1912 (1960).
(3) S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.* (London), **12**, 265 (1958).

been proposed for this difference, and it was most recently discussed by Pearson[4] in terms of the preference of a hard acid for a hard base and a soft acid for a soft base. Jørgensen[5] suggests that a given metal in either high or low oxidation state may exhibit M–SCN bonding, whereas in an intermediate oxidation state the bond type may be M–NCS.

Turco and Pecile[6] made the interesting and significant observation that for a given M, the type of bonding (M–SCN or M–NCS) depends on the nature of the other ligands in the complex (Table I). That com-

TABLE I
EFFECT OF LIGANDS ON THE TYPE OF BONDING, M–SCN OR M–NCS, FOR ANALOGOUS METAL COMPLEXES

| No. | M–SCN complexes | Ref. | No. | M–NCS complexes | Ref. |
|---|---|---|---|---|---|
| 1 | $Pt(NH_3)_2(SCN)_2$ | a | 2 | $Pt(P(C_2H_5)_3)_2(NCS)_2$ | a |
| 3 | $Pd(NH_3)_2(SCN)_2$ | a | 4 | $Pd(P(C_2H_5)_3)_2(NCS)_2$ | a |
| 5 | $Pd(Sb(C_6H_5)_3)_2(SCN)_2$ | b | 6 | $Pd(P(C_6H_5)_3)_2(NCS)_2$ | b |
| 7 | $Pd(\gamma\text{-pic})_2(SCN)_2$ | b | 8 | $Pd(py)_2(NCS)_2$ | b |
| 9 | $[Pd(dien)SCN]^+$ | c | 10 | $[Pd((C_2H_5)_4dien)NCS]^+$ | c |

$^a$ Reference 6. $^b$ J. L. Burmeister, doctorate thesis, Northwestern University, Evanston, Ill., 1964. $\gamma$-pic = $\gamma$-picoline; py = pyridine. $^c$ W. H. Baddley, doctorate thesis, Northwestern University, Evanston, Ill., 1964. dien = $NH_2C_2H_4NHC_2H_4NH_2$; $(C_2H_5)_4dien = (C_2H_5)_2NC_2H_4NHC_2H_4N(C_2H_5)_2$.

plexes of Pd(II) and Pt(II) containing $NH_3$ are of the type M–SCN, compared with analogous $P(C_2H_5)_3$ systems being M–NCS, was explained on the basis of the $\pi$-bonding of the phosphine. Wojcicki and Farona[7] have recently prepared several substituted manganese carbonyl compounds containing Mn–SCN and Mn–NCS. It was suggested that the basicity of the ligands in these systems may play an important role in determining the nature of $SCN^-$ bonding. Further study[8] indicates that steric factors may also be important.

The importance of steric factors on the nature of $SCN^-$ linkage in metal complexes has not previously been discussed in the literature. Hence, we wish to report the synthesis of the complex $[Pd((C_2H_5)_4dien)NCS]^+$ in which the Pd–NCS bonding is believed to be determined by steric factors. The compound $[Pd((C_2H_5)_4dien)NCS]SCN$ was prepared by treating an aqueous solution of $[Pd((C_2H_5)_4dien)Cl]Cl^9$ with excess KSCN at room temperature. Cooling the solution in an ice bath caused a light yellow solid to separate. This substance was recrystallized from warm aqueous ethanol. *Anal.* Calcd. for $PdC_{14}H_{29}N_5S_2$: C, 38.39; H, 6.67. Found: C, 38.59; H, 6.63. The conductivity of a 0.001 $M$ solution in water is 91 ohm$^{-1}$ mole$^{-1}$. The ultraviolet absorption spectrum shows a maximum at 325 m$\mu$ with $\epsilon = 1360$ l. mole$^{-1}$ cm.$^{-1}$. The infrared spectrum is consistent with an M–NCS linkage due to absorptions at 832 and 2100 cm.$^{-1}$ in a Nujol mull, corresponding to the C–S and C–N stretch-

(4) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).
(5) C. K. Jørgensen *Inorg. Chem.*, **3**, 1201 (1964).
(6) A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).
(7) A. Wojcicki and M. F. Farona, *Inorg. Chem.*, **3**, 151 (1964).
(8) A. Wojcicki and M. F. Farona, Paper presented at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964.
(9) W. H. Baddley and F. Basolo, *J. Am. Chem. Soc.*, **86**, 2075 (1964).

ing modes, respectively. The previously reported complex[10] [Pd(dien)SCN]NO$_3$ is S-bonded, having a weak absorption at 714 cm.$^{-1}$ in Nujol.

That Pd–NCS bonding occurs in [Pd((C$_2$H$_5$)$_4$dien)-NCS]$^+$, rather than Pd–SCN as in the analogous dien complex, appears to be due to the steric hindrance caused by the four ethyl groups. This results from the fact that the steric requirements of M–SCN bonding are greater than for M–NCS. The latter is usually linear whereas M–S–C is angular in M–SCN.[11] Molecular models show that in [Pd((C$_2$H$_5$)$_4$dien)NCS]$^+$ the linear Pd–NCS is readily accommodated but that an angular Pd–SCN would experience considerable steric strain.

A small sampling of the effect of ligands on the nature of SCN$^-$ bonding in Pd(II) and Pt(II) complexes is shown in Table I. Starting with the fact that these metal ions are of the class b type and give M–SCN, it is of interest to consider the properties of the ligands that promote M–NCS bonding. The electronic properties of the ligand have been discussed in terms of a good π-bonding ligand tending to promote M–NCS bonding.[6] This seems adequate for compounds 2,

(10) F. Basolo, H. B. Gray, and R. G. Pearson, *J. Am. Chem. Soc.*, **82**, 4200 (1960).

(11) J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 4590 (1961). Large bond angles for M–N–C of about 160° are known for some M–NCS systems in the solid state.

4, 6, and 8 but cannot account for 10. Since (C$_2$H$_5$)$_4$-dien does not π-bond, steric factors are perhaps the controlling feature in this complex. This suggests that steric factors may also contribute to the M–NCS bonding in the other systems as well. It is difficult to assess the contributions of electronic and steric factors in the compounds 2, 4, and 6 relative to 1, 3, and 5, respectively, but it should be noted that both factors operate in the same direction. Because of the large size of Sb the three phenyl groups are further removed from Pd(II) in 5 than 6, which means that the steric effect of Sb(C$_6$H$_5$)$_3$ is smaller than that of P(C$_6$H$_5$)$_3$. The steric factors at Pd(II) for 7 and 8 are identical. This shows that electronic effects are important and suggests that small effects are often all that is required to alter the nature of SCN$^-$ bonding in these systems.

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# Book Reviews

**Magnetism, A Treatise on Modern Theory and Materials.** Volume III. By GEORGE T. RADO and HARRY SUHL. Academic Press, Inc., 111 Fifth Ave., New York 3, N. Y. 1963. xv + 623 pp. 15 × 22 cm. Price, $18.00.

This is the first published volume of a three-volume series which claims to present a comprehensive summary of the present knowledge of magnetically concentrated materials. The series is written essentially for readers with a background of chemical physics, but certain sections must bring themselves to the attention of many inorganic chemists. The materials in which magnetic exchange interactions are important are mostly the alloys and the binary and ternary compounds of the transition elements.

The most pertinent chapter from the present point of view is that by J. B. Goodenough. To a certain extent, this chapter is a condensation of that author's recent book "Magnetism and the Chemical Bond" (Interscience, 1962). Here the structural features of the oxides, simple and mixed, and the halides and some other salts of the transition elements are outlined. The description of the anion packing in spinels, perovskites, garnets, etc., is quite lucidly presented. There follows a brief and rather cryptic account of parts of the theory of atomic spectroscopy, magnetic exchange interaction, and ligand field theory. While some space devoted to defining concepts is valuable, the attempt to deal with these complex subjects in a few pages is pointless. The chapter then proceeds to describe the relationship between structural features and exchange interaction propagated by "superexchange." It is shown that the symmetry of orbital overlap predicted by ligand field theory in many cases provides the basis for superexchange coupling between magnetic ions.

The relationship between the Jahn–Teller effect and the lowering of symmetry in magnetically ordered materials is brought out.

The chapter by J. S. Smart, on the evaluation of exchange integrals from experimental data, also is of some interest to an inorganic chemist. This is largely because the author deals with magnetic interactions which occur in small polymeric molecules as well as those in the more conventional "lattice" type antiferromagnetics. The exchange in Cu$_2$(CH$_3$COO)$_4$·2H$_2$O and the trimeric iron and chromium basic substituted carboxylates, for instance, is discussed. Also, exchange in systems in which the magnetic interactions are reduced by isomorphous dilution is described. Attention is drawn to the evaluation of both the "nearest neighbor" and "next nearest neighbor" exchange integrals in the more complicated systems.

The final chapter concerns the preparation of magnetically concentrated materials, mainly of the mixed oxide type. The effect of sintering on the magnetic properties is outlined. Of somewhat more interest are descriptions of methods for obtaining single crystal specimens. Flame fusion and hydrothermal synthesis techniques and results are discussed. However, most of this material is available in more extensive form in recent reviews on synthetic gemstone materials.

The remainder of the book is directed essentially at the physics of the subject. Topics include exchange in small particles and thin films, domain theory, and neutron scattering.

The book is generally well presented, and a good balance between the styles of the contributors has been maintained by the editors. Errors are not numerous, but some indicate a rather hasty preparation of manuscripts. On p. 51, there is reference to the location of oxygen positions in MnF$_3$. Figure 7 (p. 78) con-