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Preparation, Characterization and Lewis Basicity of Some Copper(II) and Nickel(II) Adducts with Organic Isocyanates and Isothiocyanates

J. F. VILLA

Department of Chemistry, H. H. Lehman College of the City University of New York, Bronx, New York 10468, U.S.A.

H. B. POWELL

Department of Chemistry, Eastern Kentucky University, Richmond, Kentucky 40475, U.S.A.

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A series of coordination compounds of RNCX ($R = CH_3, C_2H_5, C_6H_5$; $X = O, S$) with nickel(II) and copper(II) was synthetized. X-Ray powder patterns and decomposition studies demonstrated the entity of these adducts as new compounds. Infrared spectroscopy indicated that the RNCO tend to coordinate via the nitrogen atom while the RNCS tend to coordinate via the sulfur atom. UV–VIS–near IR spectroscopy studies established that the RNCX ligands are located in the low region of the spectrochemical series and their relative strength is: $C_6H_5NCO < C_6H_5NCS < CH_3NCO < CH_3NCS$.

Introduction

The organic isocyanates and isothiocyanates, RNCX ($R = CH_3, C_2H_5, C_6H_5$, $X = O, S$), appear to be versatile Lewis bases [1] because of the different possible coordination sites and the large variety of organic moieties that can be placed in the R position. However, relatively few attempts towards a better understanding of the chemistry of these molecules are in the literature, probably because of the extreme reactivity of the RNCX molecules with common solvents (including H_2O) and because of their lachrymatory properties.

The rubber industry has been issued several patents on the use of RNCX with aluminum oxide and silicon oxide [2] and with manganese(II), zirconium(IV) and copper(II) [3] (all mixed complexes with salicylaldehyde or other ligands). The data included melting points and colors and was very sketchy. Adducts of RNCS and iodine [4] and phenol [5] have been observed in solution. More recently, a nebulous compound with stoichiometry $Fe_2(CO)_7(C_6H_5N)_2$ was proposed [6–8]. Also, adducts have been formed [9] between RNCX and $TiCl_4$ and studied via infrared. It was not until 1967 that G. Wilkinson prepared [10–12] a series of RNCS with platinum and rhodium and made a thorough study of the coordination of these adducts by infrared spectroscopy. We want to report now the preparation of series of new compounds of RNCX with copper(II) and nickel(II), their characterization and elucidation of their Lewis base activity by means of infrared, X-ray, thermal decomposition and UV–VIS–near IR spectroscopy.

Experimental

Metal analyses were carried out by published methods using EDTA or DMG as complexing agents. The halogens were determined gravimetrically as the silver salts. Carbon, hydrogen and nitrogen were carried out by P.C.R., Inc., Gainesville, Florida. Some of the analyses reflect the thermal instability of the compounds prepared here; still the analyses of others were not attempted for the same reasons. Water was monitored throughout this work by means of the stretching band at approximately 3500 cm^{-1} or the deformation at 1640 cm^{-1}. It was found that the 3500 cm^{-1} band was more sensitive to traces of H_2O, but that the 1640 cm^{-1} band was better for quantitative work, being reproducible to 3% by direct comparison with standards. The X-ray powder patterns were obtained using a Philips Norelco diffractometer and CuKα radiation. The infrared spectra were obtained in a Beckman IR-10 and the UV–VIS spectra in any one of a Spectronic 505, Hitachi-Perkin-Elmer 139 or Cary 14 spectrometers. Vapor phase chromatographies were carried out in standard equipment with ten feet column of 20% carbowax on chromosorb P-20/60 mesh at 30 °C and 20 psi of helium. The decomposition studies were carried out using our own glassware closed to the atmosphere and DTA apparatus [13]. All the preparative reactions were carried out in a glove bag under dried nitrogen.

Nickel Complexes

Bis(perchlorato)bis(acetonitrile)nickel(II) was prepared according to the literature [14]. As a prelim-

TABLE I. Crystallographic Data[a] for the Adducts.

$Ni(ClO_4)_2\cdot 2CH_3CN\cdot CH_3NCO$	$NiCl_2\cdot C_6H_5NCS$	$2(CuBr_2)\cdot C_6H_5NCS$
6.865 (vw)	11.57 (s)	11.78 (vs)
5.853 (w)	7.543 (vw)	7.118 (vw)
5.216 (m)	5.853 (s, b)	5.631 (vs)
4.929 (m)	4.864 (vw)	3.543 (vs)
4.578 (w)	3.813 (w)	3.004 (s)
3.801 (s)	3.350 (vw)	2.590 (w)
3.339 (vw)	2.953 (w)	2.486 (w)
2.921 (vw)	2.520 (w)	2.307 (m)
2.627 (vw)	1.956 (vw)	2.231 (m)
2.274 (vw)	1.760 (w)	2.010 (m)
	1.721 (w)	1.976 (s)
		1.824 (m)

[a] Interplanar distances, in Angstroms; the intensities were estimated visually (s, strong; m, medium; w, weak; v, very; b, broad).

inary step, samples of the organic isocyanates and isothiocyanates were mixed with solid bis(perchlorato)-bis(acetonitrile)nickel(II) and the visible spectra of the supernatant liquids were obtained. In all cases, except with phenyl isocyanate, there was an interaction yielding a solvated nickel(II) species.

Bis(perchlorato)bis(acetonitrile)(methylisocyanate)-nickel(II)

Bis(perchlorato)bis(acetonitrile)nickel(II) (0.1 g) was placed in liquid methyl isocyanate (5 ml) and allowed to stand for 0.5 hours with occasional stirring. The colorless supernatant methyl isocyanate turned light green and was decanted leaving a wet solid residue which was dried in a stream of dry nitrogen to a powdery, light green solid, m.p. 130–170 °C decomp. *Anal.* Calcd. for $Ni(ClO_4)_2\cdot 2CH_3CN\cdot CH_3NCO$: Ni, 14.80; C, 18.14; H, 2.28; N, 10.59. Found: Ni, 14.90; C, 18.84; H, 2.81; N, 11.26.

Interaction of bis(perchlorato)bis(acetonitrile)-nickel(II) with methyl isothiocyanate

This reaction was carried out at about 40 °C because the methyl isothiocyanate ligand is solid at room temperature. A change of color to light green was observed immediately upon mixing but only a yellow solid containing chloride ion was obtained. If the reaction was carried out at higher temperatures, the redox reaction became violent and an explosion occurred.

Interaction of bis(perchlorato)bis(acetonitrile)-nickel(II) with phenyl isothiocyanate

Again an immediate change in color was observed, but no product could be isolated by adding anhydrous tetrahydrofuran nor by concentrating the solution by means of a stream of N_2 or the use of a vacuum.

Interaction of bis(perchlorato)bis(acetonitrile)-nickel(II) with phenyl isocyanate

No reaction was apparent when bis(perchlorato)-bis(acetonitrile)nickel(II) and phenyl isocyanate were mixed. Decantation and infrared analysis confirmed the unreacted state of the phenyl isocyanate.

Interaction of $NiCl_2$ anhydrous (a.) with organic isothiocyanate

No reaction was observed at room temperature but upon refluxing 1.5 g of anhydrous $NiCl_2$ and 20 ml of phenyl isothiocyanate in an apparatus closed to air for 24 hours a black solid was obtained. Decomp. 30 °C. *Anal.* Calcd. for $NiCl_2\cdot C_6H_5NCS$: Ni, 22.18. Found: Ni, 22.50. The aliphatic counterpart yielded decomposition products.

Interaction of $NiCl_2$ with organic isocyanates

Again no reaction was observed at room temperature but upon refluxing $NiCl_2$ with phenyl isocyanate, a solid, unstable above –20 °C, was obtained. *Anal.* Calcd. for $NiCl_2\cdot C_6H_5NCO$: Ni, 23.60. Found: Ni, 26.42. When the same reaction was carried out with methyl isocyanate, only methyl isocyanate trimer was obtained as product.

Copper Complexes

As a preliminary step, $CuBr_2$ (a.) was mixed with methyl isocyanate, phenyl isocyanate, ethyl isothiocyanate and phenyl isothiocyanate at room temperature. A reaction was evident immediately in all cases.

(a) Further attempts to isolate new coordination compounds with the isocyanates yielded only starting materials or methyl isocyanate trimer.

(b) No solids could be isolated with the isothiocyanates but refluxing about 4 g of $CuBr_2$ (a.) in 25 ml of phenyl isothiocyanate yielded a precipitate by addition of methyl cyclohexane (a.). Decomposition temperature approximately 0 °C. *Anal.* Calcd.

TABLE II. Infrared Data of the Adducts.[a]

Compound	ν_{as} (NCX)	ν_{sym} (NCX)	ν (anions)
CH_3NCO	2270	1412[b]	–
C_6H_5NCS	2100 (b)	927	–
$Ni(ClO_4)_2 \cdot 2CH_3CN \cdot CH_3NCO$	1850		1205 (s)
	1750	–	1135 (sh)
	1680 (b)		1110 (s)
			1030 (sh)
			1000 (s)
			100
$TiCl_4 \cdot 2CH_3NCO$[c]	1845		
	1750	–	–
	1650		
$NiCl_2 \cdot C_6H_5NCS$	2060 (b)	930	300
$Rh(Ph_3P)_2 \cdot 2C_6H_5NCS \cdot Cl$[d]	2155 and 1540	925	–
$CuBr_2 \cdot 2C_6H_5NCS$	2160		
	1680	–	–
	1595		
$2(CuBr_2) \cdot C_6H_5NCS$	1670	800	300
	1500 (b)		
$Pt(Ph_3P)_2 \cdot C_6H_5NCS$[c]	1643	782	–
	1582		

[a] The following notation is used: s, strong; b, broad; sh, shoulder. [b] Taken from reference 18. [c] Taken from reference 9. [d] Taken from reference 10.

for $CuBr_2 \cdot 2C_6H_5NCS$: Cu, 12.8. Found: Cu, 11.5. The solid residue of the reaction had a different stoichiometry. *Anal.* Calcd. for $2(CuBr_2) \cdot C_6H_5NCS$: Cu, 21.9. Found: 22.8. Decomp. 50 °C. Attempts to prepare the 1:1 adduct were not successful. It should be noted at this point that an additional large variety and quantity of reactions were carried out, such as using UV radiation to enhance the reaction, or stronger reflux, *etc.*, but only those reactions that yielded discernable results were described above.

Results and Discussion

Identification (VPC and IR) of the gases evolved from these coordination compounds upon thermal decomposition indicated that the ligands were coordinated as a unity, that is, without any internal rearrangement or decomposition. The X-ray powder patterns of the more stable of these compounds are shown in Table I, where the interlattice spacings in A and a visual estimate of the intensity of the arcs are listed. These spacings were different to the respective starting materials indicating the entity of the new compounds.

Probably the best method of determining the place of coordination of the ligands in these coordination compounds (short of single crystal work) is the study of the shifts encountered in the infrared spectra of the ligands upon coordination. The three expected stretching modes of the organic isocyanates and isothiocyanates have been approximated [15–17] as the R–N stretch, ν(RN), the N–C stretch, ν(NC), and C–X stretch, ν(CX). These three modes would be expected to interact and mix with each other because of the extensive π system and because of the similarity in energy. In particular, the N–C stretch and the C–X stretch are known to be highly mixed and indeed have been labeled [15–17] NCX asymmetric stretch, ν_{as}(NCX) and NC symmetric stretch, ν_{sym}(NCX), respectively, to emphasize the mixing. The infrared data obtained on these coordination compounds are shown in Table II. The free ligands have the ν_{as}(NCX) in the 2300–2000 cm^{-1} region which indicates that cannonical structure (II) is predominant.

$$R{-}N{=}C{=}X \text{ (I)} \rightarrow R{-}N^{+}{\equiv}C{-}X^{-} \text{ (II)}$$

The C–X stretch, ν_{sym}(NCX), present in the 900 cm^{-1} region for the organic isothiocyanates [17, 18] and in the 1300–1400 cm^{-1} region for the organic isocyanates [19] should also be sensitive to the Lewis base activity, and characteristic of the place of coordination. Unfortunately, in the organic isocyanate and isothiocyanate systems, the ν_{sym}-

TABLE III. Visible Spectra and Ligand Field Parameters[a] of Bis(perchlorato)bis(acetonitrile)nickel(II) in the Organic Isocyanates and Isothiocyanates

Ligand	λ_{max} for $^3A_{2g}$				D_q Total	D_q Ligand	B^c	β
	$^3T_{1g}(P)$	$^3T_{1g}(F)$	^1E_g	$^3T_{2g}{}^b$				
CH_3NCO	25000	15500	14900(sh)	–	895	845	775	0.75
CH_3NCS	25640	14920	–	–	940	980	795	0.77
C_6H_5NCO	–	–	–	–	–	–	–	–
C_6H_5NCS	25000	15260	–	–	860	740	860	0.83
CH_3CN^d	25000	14500	13700(sh)	8750	875	1060	884	0.85

[a] All units are in cm^{-1}. [b] The $^3T_{2g} \leftarrow {}^3A_{2g}$ transition was outside the range of our spectrometer. [c] B_0 for free nickel(II) is 1040 cm^{-1}. [d] Taken from reference [14].

(NCX) bands are overshadowed and frequently hidden by phenyl group breathing modes or by methyl deformation modes. Further, the ν_{sym}(NCO) for the organic isocyanates is generally a weak band [20]. ν_{sym}(NCX) is then a much less useful diagnostic tool but will be used whenever possible. In bis(perchlorato)bis(acetonitrile)(methylisocyanate)nickel(II) the ν_{as}(NCO) band has shifted down to the 1800–1700 cm^{-1} region. The band has broadened and appears complex; however, little significance can be attached to this complexity since several overtones and combination bands appear in this region. The shift indicates that the bond order between the nitrogen and carbon atoms has decreased, that cannonical (I) is predominant and that the coordination is through the nitrogen atom. ν_{sym}(NCX) could not be assigned. A similar spectrum has been observed in bis(ethyl isocyanate)titanium(IV) chloride [9] which is coordinated through the nitrogen atom.

In dichloro(phenyl isothiocyanate)nickel(II) ν_{as}(NCS) is at 2060 cm^{-1} and ν_{sym}(NCS) at 930 cm^{-1}, only slightly shifted from the uncoordinated ligand suggesting ligation through the sulfur atom and similarity to the coordination of one of the phenyl isothiocyanates molecules in the previously studied [10] bis(triphenylphosphine)bis(phenyl isothiocyanate)rhodium(I) chloride. For the tetrabromo (phenyl isothiocyanate)dicopper(II) coordination compound ν_{as}(NCS) has shifted down to the 1600–1500 cm^{-1} region, indicating possible coordination at the C–S atoms. The band at 800 cm^{-1} is assigned to the ν_{sym}(NCS) which indicates a shift from the 927 cm^{-1} position in the uncoordinated ligand and corroborates the coordination mode above postulated. This type of coordination has been observed by Wilkinson, *et al.* [10] in bis(triphenylphosphine)phenyl isothiocyanateplatinum(0), which absorbs in the same regions as the copper compound prepared here. Finally, the $CuBr_2 \cdot 2C_6H_5NCS$ seems to possess two kinds of phenyl isothiocyanate, one sulfur coordinated and one C–S coordinated, similar to the rhodium(I) compound [10]. However, in this case the apparently sulfur coordinated ligand could be uncoordinated ligand produced by decomposition of the adduct.

In general, the sulfur atom of these organic molecules acted as the donor atom in reactions with copper(II) bromide and nickel(II) chloride, even though nickel(II) chloride is usually considered a hard acid in the Pearson sense [21, 22] while the nitrogen atom was almost exclusively the donor atom with the harder bis(perchlorato)bis(acetonitrile)-nickel(II). This apparent extra basicity, even with hard acids, of the sulfur atom when compared to the nitrogen atom, is probably a result of the additional "free" lone pair on the sulfur atom. The "lone pair" on the nitrogen atom is partially used in π bonding within the –NCX group. It is only when the hardest metal salt is used that the hard nitrogen has the capability of forming a solid adduct stable at room temperature.

The metal halide stretch in these coordination compounds were too broad to be used in any useful correlation, but they were located in the same general area as the free metal halides, possibly indicating a polymeric nature.

The perchlorato absorption in the bis(perchlorato)bis(acetonitrile)(methyl isocyanate)nickel(II) (Table II) indicates [14, 23] that there is one perchlorate group acting as monodentate with bands at 1135 and 1012 cm^{-1} and one acting as bidentate with bands at 1205, 1110 and 1000 cm^{-1}. The solution infrared spectrum using methyl isocyanate as the solvent suggested the presence of only monodentate perchlorate groups, with a strong band at 1020 cm^{-1} (the band at 1135 cm^{-1} was masked by solvent) and with the band at 1205 cm^{-1} clearly absent. It is possible that the bidentate perchlorate group was converted to monodentate by additional methyl isocyanate coordination.

The general base strength of these ligands was investigated by means of UV–VIS spectroscopy. Table III has the λ_{max} positions of solutions of bis(perchlorato)bis(acetonitrile)nickel(II) in each of these ligands. The spectra were interpreted as a $^3A_{2g}$ ground state with octahedral configuration. A semi-quantitative Tanabe–Sugano analysis [24, 25] of the data yielded the values of D_q, B and β shown in Table III. Jorgensen's rule [26] of averaging environments was used with a value [14] of 1060 cm^{-1} for CH_3CN and of 780 cm^{-1} for the monodentate perchlorate anion [14, 27]. The observed order of D_q is $CH_3NCS > CH_3NCO > C_6H_5NCS > C_6H_5NCO$ with the whole sequence in the low end of the spectrochemical series. This trend can be rationalized if it is remembered that the coordination is via the nitrogen atom. The larger size of the phenyl group compared to the methyl group would lead to greater steric hindrance and a smaller ligand field. Also, the electron donating ability of the methyl group would make the electron pair on the nitrogen of the methyl compounds more available for donation. The greater electron withdrawing ability of oxygen compared to sulfur would decrease the Lewis base donor ability of methyl isocyanate and phenyl isocyanate compared to the sulfur analogs. Because the organic groups are attached directly to nitrogen, their effect might be greater than the effect of oxygen or sulfur. This is indeed what is observed. The phenyl compounds are considerably weaker donors than the methyl compounds while there is less difference between the oxygen and sulfur analogs. The same type of discussion applies to the β values obtained in this investigation, but they were not as definitive as the D_q values.

The same types of experiments were carried out in the visible region with solutions of $CuBr_2$ in the organic isocyanates and isothiocyanates. The positions of λ_{max} are shown in Table IV. The spectra looked similar to each other and each contained bands in the 400 and 640 nm ranges. The intensity of the bands seemed to indicate that they were charge transfer in origin. The previously reported [28] spectrum of $CuBr_2$ in acetonitrile also had charge transfer bands near 400 and 640 nm, in addition to bands in the UV region. In order to complete the comparison, the UV spectrum of the methyl isocyanate system was also obtained. It contained bands in approximately the same places as the acetonitrile system, see Table IV. In light of the great similarities, we propose a similar interpretation for our systems than that of the acetonitrile system, that is, a $CuBr_3^- \cdot 2L$ species of C_{3v} symmetry. This species would have a ligand π orbital representation of A_1, A_2 and 2E while the metal d orbitals would be A_1 and 2E giving rise to four charge transfer bands, one of them a π non-bonding metal d transition and the other three π bonding-metal d transitions, in agreement with the experimentally found bands. It should be noted that a *cis*-$CuBr_3^- \cdot 3L$ species would also fit the proposed pattern. The near infrared region [29] was also scanned in the methyl isocyanate solution in order to look for d–d transitions and two bands were found. The one at about 900 nm can be assigned to the d–d transition of the above mentioned species and the one at about 1200 nm to a completely solvated Cu^{++} species, $Cu^{++} \cdot 6L$. The D_q value obtained from this band for the methyl isocyanate ligand is 835 cm^{-1} in agreement with the 835 cm^{-1} value obtained in the previous experiments reported above. This indicates that the highly electronegative oxygen atom does not play an important role in the coordination of these compounds.

TABLE IV. Ultraviolet–Visible Data for Copper(II) Bromide in the Organic Isocyanates and Isothiocyanates.

Ligand (Solvent)	λ_{max} (mμ)
Acetonitrile[a]	265, 360, 425, 640
Methyl Isocyanate	230, 355, 430, 630, 900, 1200
Phenyl Isocyanate	380–390, 640
Phenyl Isothiocyanate	400, 650

[a] Data taken from reference 29.

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29 The spectrum was obtained in a Cary 14 spectrophotometer, using sealed Pyrex tubes as cuvettes through the courtesy of Dr. L. S. Dietrich and Miss B. R. Farinas of the University of Miami Medical Research Center.