CCl_4 was used for each 26 ml. of tube volume, *i.e.*, 32 to 40 ml. of CCl_4 was used.[2] The sealed glass tube was placed in a steel bomb into which was also added 8 ml. of CCl_4 for each 26 ml. of void space to balance the pressure in the tube. The temperature was held to 400° for a period ranging from 2 to 4 hr. Products were handled in a drybox.

Analysis.—Tungsten was determined gravimetrically as WO_3, chlorine as AgCl, and rhenium as $(C_6H_5)_4AsReO_4$. Iron was titrated with Ce(IV). Molybdenum was determined by reduction to Mo(III), oxidation with Fe(III), and back titration of the iron Fe(II) formed with Ce(IV).

Products. (a) **WCl_6.**—Five grams of WS_3 gave 6.8 g. of WCl_6 (85% yield) and 0.8 g. of WS_3 gave 0.8 g. of WCl_6 (70% yield).

Anal. Calcd. for WCl_6: W, 46.4; Cl, 53.6. Found: W, 45.9 ± 0.1; Cl, 53.4 ± 0.1; Cl/W, 6.05.

(b) **$MoCl_5$.**—About 2.6 g. of MoS_3 gave 2.8 g. (80% yield) of $MoCl_5$. The best yield was obtained when 1 g. of MoS_2 was allowed to react for 12 hr.; 3% acid-insoluble residue remained.

Anal. Calcd. for $MoCl_5$: Mo, 35.1; Cl, 64.9. Found: Mo, 35.1 ± 0.1; Cl, 64.7 ± 0.1; Cl/Mo, 4.97.

(c) **$ReCl_5$.**—About 1.5 g. of Re_2S_7 after 10 hr. heating in the bomb gave 1.5 g. of $ReCl_5$ (80% yield).

Anal. Calcd.: Re, 51.2; Cl, 48.8. Found: Re, 50.8 ± 0.2; Cl, 47.0 ± 0.1; Cl/Re, 4.86.

(d) **$FeCl_3$.**—Four grams of FeS_2 gave 5.3 g. of $FeCl_3$ after 8 hr. heating in the bomb; 10% of acid-insoluble residue remained; Cl/Fe found, 3.02. Three grams of FeS gave 5.4 g. of $FeCl_3$ after 12 hr. heating in the bomb; 4% of an acid-insoluble residue remained; Cl/Fe found, 3.01.

Discussion

The advantages of this method are that: (1) Anhydrous metal chlorides are directly prepared from the sulfides, either synthetic or natural. (2) Under the conditions of the experiment usually the metal is converted to a single chloride rather than a mixture of chlorides and/or oxide chlorides. (3) Where sand is the only significant contaminant, as from certain ores, if the metal chloride is to be carried through further reaction steps, then no purification is indicated. However, if the pure metal chloride is the objective of the process it can be separated from the admixed solid usually by sublimation or extraction with an inert solvent, such as CCl_4, appropriate to the particular metal chloride. (4) It appears that many sulfides will prove to be as easily converted to the metal chlorides by this method as the corresponding oxides and some may, indeed, be more readily converted. (5) The more ready availability of some of the sulfides, *e.g.*, the MoS_2 used in this work, as compared to the oxides indicates inherent simplification of any process requiring ultimately the anhydrous chloride. (6) The method is a straightforward, single-step manipulation for solubilizing and extracting metals from their sulfide ores.

Correspondence

Infrared Spectral Evidence of π-Bonding in the $Fe(CN)_5NO^{-2}$ Ion

Sir:

Recently, Ballhausen and Gray[1] have derived a rule for octahedral distorted complexes of tetragonal symmetry (ML_5X), in which they state that almost all the π-bonding is axially directed and involves the metal d_{xz} and d_{yz} orbitals, the d_{xy} being approximately a nonbonding orbital. Following the above rule in the case of $M(CN)_5NO$ complexes, they arrived at the conclusion that the M–NO bond order was unusually high; there is strong M–NO π-bonding and therefore the pentacyanonitrosyls are not octahedral.

One of us[2] arrived at similar conclusions by measurements of the Mössbauer effect in the case of $Fe(CN)_5NO^{-2}$. Herington and Kynaston,[3] using infrared spectroscopy in the region of the antisymmetric stretching of the CN bond, have called attention to the striking difference existing between the nitroprusside and some other pentacyano complexes of iron. In the present work we have extended the infrared spectroscopic data to other $Fe(CN)_5X$ complexes in the region of the CN (ν_6) and MC (ν_7 and ν_8) stretching vibrations.

As can be seen in Table I, the frequencies of the CN and MC bands depend on the charge of the central ion and are independent of the charge of the X group with the exception of $Fe(CN)_5NO^{-2}$. All the spectra of Fe^{II} compounds exhibit a very strong and broad band at 2040–2060 cm.$^{-1}$ and those of Fe^{III} compounds a strong and narrow band at 2120–2130 cm.$^{-1}$ assigned to the antisymmetric stretching vibration of the CN group. On the other hand, in the spectra of Fe^{II} compounds there are two absorptions in the KBr region, one at 570–580 cm.$^{-1}$ and the other at 400–420 cm.$^{-1}$. These two absorptions are shifted to 495–535 and 390–400 cm.$^{-1}$, respectively, in the spectra of Fe^{III} compounds. It has been shown[4] that the higher of the two absorptions (ν_7) is mainly associated with MCN bending and the lower one (ν_8) with MC stretching. Although there is some mixing of the two modes in these vibrations, it is worth noting that the higher one shows the most marked shifts in passing from the Fe^{II} to the Fe^{III} pentacyano complexes, as might be expected of the vibration which is mainly associated with the stretching mode. Qualitatively, we also confirmed the previous observation that the intensity of the CN band in Fe^{II} complexes is about two times that in Fe^{III} complexes.

The position of the MC and CN stretching bands and the intensity of the latter can be explained on the basis of the ideas of Jones.[5] Investigating the hexacyanometal complexes, this author concludes that the

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(1) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **2**, 426 (1963).

(2) J. Danon, *J. Chem. Phys.*, **39**, 266 (1963).

(3) E. F. Herington and W. Kynaston, *J. Chem. Soc.*, 3555 (1955).

(4) L. H. Jones, *J. Chem. Phys.*, **36**, 1209 (1962).

(5) L. H. Jones, Proceedings, 7th International Congress on Coordination Chemistry, Stockholm, 1962.

TABLE I[a]

Fe^{II} complex	ν_6	ν_7	ν_8	Fe^{III} complex	ν_6	ν_7	ν_8
$Fe(CN)_6^{-4}$	2040 s, br	584 s	417 m	$Fe(CN)_6^{-3}$	2042 w 2078 w 2118 s	510 w	390 s, br
$Fe(CN)_5H_2O^{-3}$	2015 w 2035 sh 2045 s br 2060 sh	572 m	405 m 430 vw	$Fe(CN)_5H_2O^{-2}$	2070 w 2132 m	535 vw	400 s, br
$Fe(CN)_5NH_3^{-3}$	2000 sh 2040 sh br 2055 s	500 vw 566 s, br 580 sh	395 w 420 vw 435 vw	$Fe(CN)_5NH_3^{-2}$	2068 w 2123 s 2140 m 2150 m	518 w	405 s, br 460 w
$Fe(CN)_5NO_2^{-4}$	2060 s, br	570 s	400 s, br 425 sh	$Fe(CN)_5NO_2^{-3}$	2065 w 2080 vw 2122 s 2140 sh	498 w	403 s, br
$Fe(CN)_5SO_3^{-5}$	2052 s, br	525 w 577 s	405 m 435 sh	$Fe(CN)_5NO^{-2}$	2148 s 2160 s 2170 s	470 w 497 w 515 vw	420 s 435 sh 450 sh

[a] s, strong; m, medium; w, weak; vw, very weak; br, broad. Infrared spectra were obtained by Beckman IR-7 and Carl Zeiss UR 10 infrared spectrometers for the NaCl and the KBr regions, respectively, using the Nujol mull technique.

increase of the metal–carbon σ-bond tends to increase both the MC and CN force constants and that the increase of the metal–carbon π-bond increases the MC force constant and decreases the CN force constant. By adding one dε electron in passing from $Fe(CN)_6^{-3}$ to $Fe(CN)_6^{-4}$ there is apparently greatly increased M–C π-bonding leading to an increase in the MC force constant (ν_7 and ν_8 increase), a significant decrease in the CN force constant (ν_6 decreases), and to a considerable increase in change in CN bond moment accompanying the ν_6 vibration (the ν_6 peak absorption coefficient in aqueous solution increases 4.5 times).

Extending this interpretation to the $Fe(CN)_5X$ complexes one concludes that the position of the MC and CN stretching bands and the shape of the latter indicate more π-bonding in the metal–carbon bond in Fe^{II} than in Fe^{III} pentacyano complexes. There appears to be some effect (weakening of the M–C π-bonding) when a CN^- group is replaced by an NO_2^- group. Nevertheless, the unusually high frequency and the shape of the CN band in $Fe(CN)_5NO^{-2}$ indicate less π-bonding in the M–C bond in this compound than in any other of the pentacyano complexes studied. This might be due, as has been pointed out by Ballhausen and Gray,[1] to the presence of "heavy M–NO π-bonding." The π-bonding is axially directed toward the NO group and the compound is by no means octahedral.[6]

There is another fact which adds evidence to the statement above: the ν_6, ν_7, and ν_8 bands are of the F_{1u} species, that is, triply degenerate. In passing to a lower symmetry one might expect the disappearance of the degeneracy and the splitting of the bands into their three components. This splitting has been observed for both CN and MC stretching bands[7–9] in the case of $Fe(CN)_5NO^{-2}$. However, there is no such pronounced splitting in the bands of the other compounds. With the exception of the ν_6 band of $Fe(CN)_5NH_3^{-2}$ one observes only the appearance of some fine structure in the CN band of some complexes that can be attributed to crystal effects.

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RECEIVED AUGUST 1, 1963

Thiocyanato-S-pentacarbonylmanganese(I) and Some Derivatives

Sir:

We wish to report the first simple thiocyanato metal carbonyl, $Mn(CO)_5SCN$, and to comment on the nature of attachment of the thiocyanate ion in this and some related compounds.

Thiocyanatopentacarbonylmanganese(I) is prepared by addition of a tetrahydrofuran solution of $NaMn(CO)_5$ to a stoichiometric amount of chlorothiocyanogen (ClSCN) in tetrahydrofuran under nitrogen. After removal of the solvent under reduced pressure, the residue is extracted with chloroform and filtered. Slow addition of petroleum ether to the filtrate affords golden yellow crystals (70–80% yield). The compound, which is a nonelectrolyte in nitromethane, dissolves readily in chloroform, acetone, acetonitrile, and methanol but not in benzene, petroleum ether, carbon

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(6) There is the same evidence of π-bonding in the study of MC stretching mode in the Raman spectrum (H. Stammreich, private communication).

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