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THE He(I) PHOTOELECTRON SPECTRA AND VALENCE ELECTRONIC STRUCTURES OF η^5-$C_5H_5Mn(CO)_2N_2$ AND η^5-$C_5H_5Mn(CO)_2NH_3$

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Summary

The He(I) photoelectron spectra of η^5-$C_5H_5Mn(CO)_2N_2$ and η^5-$C_5H_5Mn(CO)_2$-NH_3 have been obtained. The general features of these spectra resemble those of the parent carbonyl complex, η^5-$C_5H_5Mn(CO)_3$. The major differences appear in the ionizations associated predominantly with the metal *d* levels, where shifts in ionization energies and loss of degeneracy reflect the differences in bonding of the nitrogen ligands and a carbonyl ligand with the metal center. Non-empirical molecular orbital calculations were used as an aid for the interpretation of these binding energy shifts. In the case of N_2 bound to the metal, the shifts in ionization potentials are predicted with extreme accuracy by the shifts in eigenvalues of the calculations. Thus the electronic structure of transition metal dinitrogen complexes, as compared to carbonyl complexes, is accurately described. The quantitative prediction of binding energy shifts for the amine complex are less satisfactory, although the qualitative behavior is reproduced quite well.

Introduction

Since the preparation of $[Ru(NH_3)_5(N_2)]^{2+}$ in 1956 [1], the synthesis and properties of transition metal complexes containing molecular nitrogen have received a considerable amount of attention [2]. Much of this interest is generated by the potential ability of transition metal complexes to chemically "fix" dinitrogen [3]. The behavior of transition metal complexes with a dinitrogen ligand is especially intriguing in comparison to the behavior of similar complexes with the more familiar ligand carbon monoxide. Theoretical calculations indicate that the orbital eigenvalues of N_2 and CO are quite similar [4]. However, because N_2 is a homonuclear diatomic molecule and CO is not, the spatial distribution of corresponding orbitals in these two molecules is not the same. The implications of these differences in structure between N_2 and CO to the relative bonding of these ligands in transition metal complexes have been investigated by a variety of methods, and many of the conclusions drawn from these studies are in conflict [5—7]. Unfortunately, until now the information obtained experimentally on dinitrogen complexes has not been capable of resolving questions concerning individual valence electronic interactions. The combined experimental and theoretical investigations of the present work address these questions directly.

A series of $CpMn(CO)_2L$ (where $Cp = \eta^5\text{-}C_5H_5$) nitrogen complexes has recently been synthesized [8—11]. These species provide an excellent opportunity to study the relative bonding of carbonyl and nitrogen ligands. The electronic structure of the analogous carbonyl molecule, $CpMn(CO)_3$, has recently been investigated via He(I) photoelectron spectroscopy and molecular orbital calculations [12]. A similar investigation concerning the dinitrogen complex, $CpMn(CO)_2N_2$, will offer direct evidence for the bonding interactions of N_2 in comparison to those of CO. Further information is obtainable from study of another nitrogen complex, $CpMn(CO)_2NH_3$, which may be compared with both $CpMn(CO)_3$ and $CpMn(CO)_2N_2$. The results for $CpMn(CO)_2NH_3$ may also be related to the results of a recent investigation [13] of a series of $M(CO)_5NR_3$ complexes which employed photoelectron spectroscopy and ab initio molecular orbital calculations.

Experimental

Photoelectron spectra

The ionization spectra of $CpMn(CO)_2N_2$ and $CpMn(CO)_2NH_3$ were measured on the Varian IEE-15 electron spectrometer in the UV configuration. Argon was used as a single internal standard. Simultaneous observation of a number of reference peaks showed that the energy scale was linear to within ±0.01 eV over a binding energy range from 9 to 17 eV. Both samples were introduced into the ionization chamber by means of the variable temperature inlet probe. The spectrum of $CpMn(CO)_2N_2$ was obtained without difficulty. The samples of $CpMn(CO)_2NH_3$ were transferred to the instrument under nitrogen. The problems associated with obtaining the spectrum of the amine complex are discussed in the results section.

In order to describe the low binding energy ionizations accurately and concisely, the bands were curve-fit with asymmetrical Gaussian peaks as described elsewhere [12]. The exact form of these peaks is:

$$C(E) = A\, e^{-k[(E-P)/W]^2}$$

where $C(E)$ = electron counts at binding energy E; A = amplitude of the peak; P = position of the peak (vertical ionization potential) $W = W_h$, the halfwidth for $E > P$; $k = 4\ln 2$, $W = W_l$, the halfwidth for $E < P$.

Calculations

The Fenske method [14] of molecular orbital calculations was used to facilitate interpretation of the photoelectron ionizations and provide further insight into the bonding in these complexes. The value and limitations of this method for interpreting the ionizations in photoelectron spectra have been discussed in other contexts [12,15]. No allowance is made in this method for variable or empirical parameters. The results of the approximate calculations are dependent only on the atomic functions and nuclear coordinates of a given molecule. The atomic functions are determined from functions for the free atoms [16], and the nuclear coordinates are chosen from the available crystal structure data [17,18]. The calculations on $CpMn(CO)_2N_2$ and $CpMn(CO)_2NH_3$ parallel the previous calculation on $CpMn(CO)_3$ [12]. For the calculation on $CpMn(CO)_2N_2$, the Mn—N and N—N distances were taken to be 1.80 and 1.10 Å respectively. The Mn—N and N—H bond distances used in the calculation for $CpMn(CO)_2NH_3$ were 2.08 and 1.06 Å respectively. In order to maintain consistency with earlier calculations, the N_2 $2\sigma_g$ and $3\sigma_u$, and the NH_3 $2a_1$ and $4a_1$ orbitals were frozen to the form determined for the isolated ligands. The details of this procedure are discussed elsewhere [19]. Perturbation theory analysis of the restricted-variation wavefunction indicates that the results are not significantly different from the results of a full-basis variation calculation.

Experimental results

The photoelectron spectrum of $CpMn(CO)_2N_2$ is shown in Fig. 1. The general features of this spectrum resemble the features observed in the spectrum of $CpMn(CO)_3$ [12]. Both spectra exhibit a broad, intense band in a binding energy range from 12.5 to 15.5 eV. In the case of $CpMn(CO)_3$, this band has been attributed to ionization from levels which are predominantly the carbonyl 5σ and 1π orbitals, the ring a_2'' orbital, and certain of the ring σ orbitals. The ionization

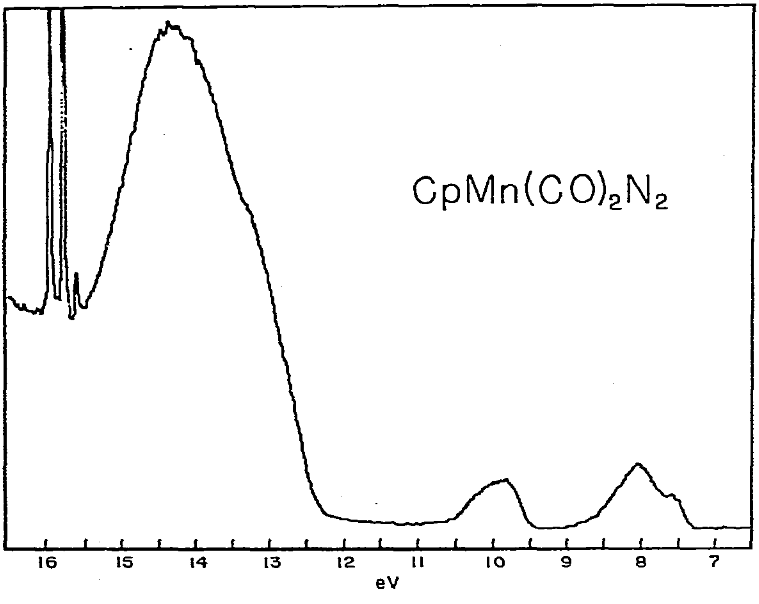

Fig. 1. The photoelectron spectrum of $CpMn(CO)_2N_2$.

bands between 7 and 11 eV were fit with asymmetric Gaussian peaks. The results of this analysis are presented in Table 1. The ionization band near 10 eV displays a definite shoulder on its high binding energy side. As in the case of CpMn(CO)$_3$, two peaks with equal shapes were used to fit this band. The shoulder is found to be lower in intensity and separated from the vertical ionization potential of this band by 0.39 eV, which is the same as that observed for the corresponding band in the spectrum of CpMn(CO)$_3$. This characteristic band shape also occurs in the spectra of several other (η^5-cyclopentadienyl)metal complexes, and has been assigned as being associated with ionization from predominantly ring e_1'' orbitals [12].

The ionization bands near 8 eV are attributed to ionizations from the levels which are primarily metal d in character. The shape of this ionization band in the spectrum of CpMn(CO)$_2$N$_2$ is substantially different from the shape of the corresponding band in the spectrum of CpMn(CO)$_3$. Whereas, in the spectrum of CpMn(CO)$_3$, a single broad band with no discernable shoulders was observed; two distinctly separate vertical ionization potentials are observed in this region in the spectrum of CpMn(CO)$_2$N$_2$. The low binding energy peak is approximately half as intense as the next peak. Three separate peaks of equal shapes and amplitudes were used to fit this band. This fit is displayed in Fig. 2. In this fit, the low binding energy peak is followed by two peaks which are close in energy. The binding energies of these latter peaks are somewhat uncertain, but may be considered to define the probable range for vertical ionization potentials in this region.

The ionization spectrum of CpMn(CO)$_2$NH$_3$ was difficult to measure. The complex is not volatile at 25° C. With mild warming of the probe, the spectrum displayed in Fig. 3 was obtained. The sharp vibrational structure observed around 11 eV in this spectrum is evidence that the complex is decomposing thermally, giving off free ammonia. The sharp ionization at 14 eV indicates that some carbon monoxide is being released also. The ionizations occurring in the binding energy range from 6.5 to 11 eV are shown in greater detail in Fig. 4. The data of the top curve were collected with the probe temperature at 60° C. This spectrum represents the combination of 8.5 h of data collection. The spectrum was measured in one hour segments, in each of which 180 scans of 20 sec duration were collected. Comparison of these individual spectra indicated that no transient behavior was occurring. Warming the probe to 80° C then produced the lower

TABLE 1

IONIZATION DATA FOR η^5-C$_5$H$_5$Mn(CO)$_2$N$_2$

Band	Ionization potential	Relative amplitude	W_h	W_l	Relative area
1,	7.54	1	0.73	0.25	1.36
1′	7.89	1 ^{a}	0.73 ^{a}	0.25 ^{a}	
1″	8.07	1 ^{a}	0.73 ^{a}	0.25 ^{a}	
2,	9.78	1.61	0.53	0.36	1
2′	10.17	0.82	0.53 ^{a}	0.36 ^{a}	

^{a} Constrained parameters.

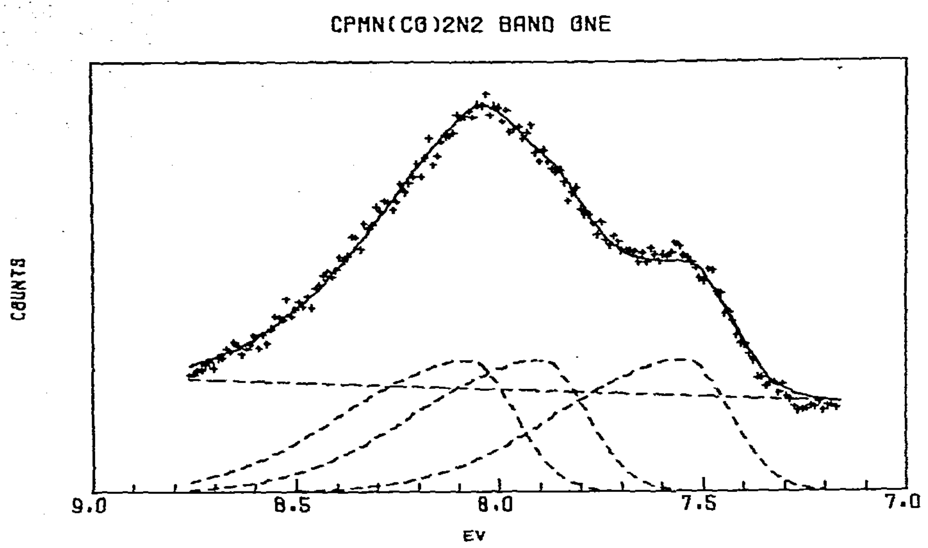

Fig. 2. The plus signs are the data values. The dashed lines are the curve fit Gaussian peaks and baseline, and the solid line is the fit sum.

spectrum in Fig. 4. The ionization bands at this temperature correspond to the ionization bands of $CpMn(CO)_3$. The thermal decomposition of $CpMn(CO)_2NH_3$ to produce $CpMn(CO)_3$ is consistent with the known decomposition of other amine complexes [20—22]. The ionization bands between 6.5 and 7.5 eV and the band between 9.0 and 9.5 eV maintain constant relative intensities with each other over the complete temperature range. Fortunately, these bands do not overlap substantially with the bands of $CpMn(CO)_3$. Subtracting the lower spectrum in Fig. 4 from the top spectrum yields the spectrum displayed in Fig. 5.

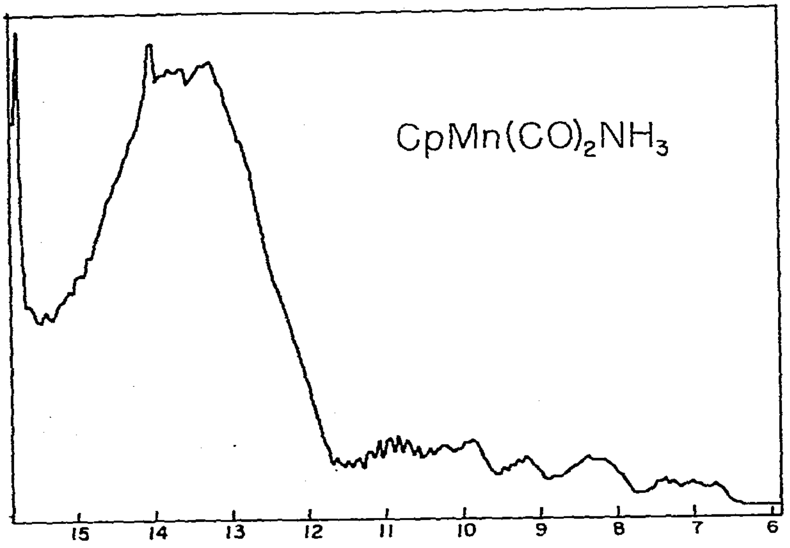

Fig. 3. The ionization spectrum of $CpMn(CO)_2NH_3$.

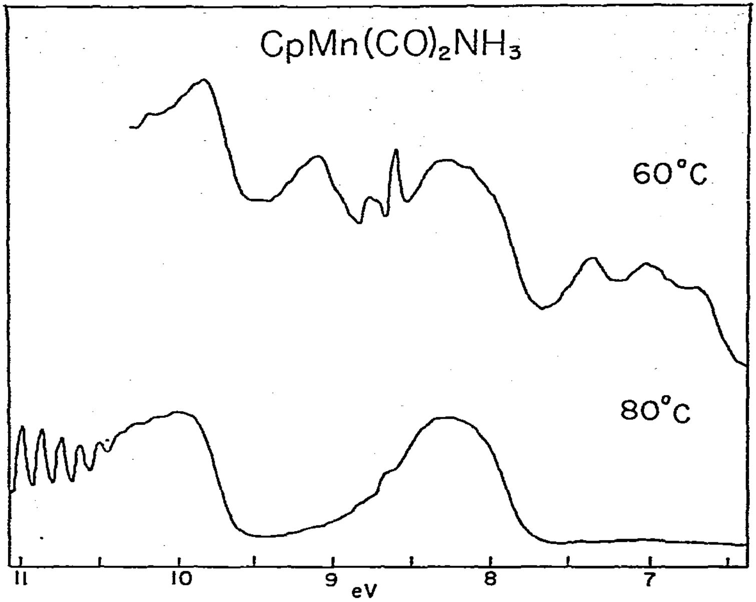

Fig. 4. The ionization spectrum of $CpMn(CO)_2NH_3$ between 6.5 to 11 eV.

This spectrum is assumed to correspond to the ionizations of $CpMn(CO)_2NH_3$. Further justification of this assumption is based upon comparison of this spectrum with the spectra of other $M(CO)_5NR_3$ complexes [13] and theoretical considerations (vide infra). The results of curve-fitting these ionization bands are presented in Table 2. The halfwidths and shape of the band at 9.15 eV are uncertain. It is interesting to note that the initial ionization of $CpMn(CO)_2NH_3$ occurs at an extremely low binding energy. The vertical ionization potential at 6.63 eV may be the lowest binding energy ever observed for a closed-shell molecule.

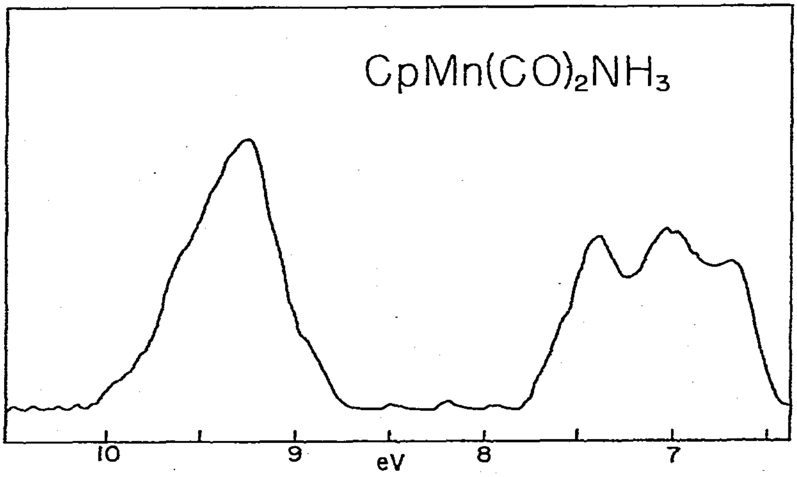

Fig. 5. Photoelectron spectrum of $CpMn(CO)_2NH_3$ at 60°C minus the ionization bands observed at 80°C.

TABLE 2

IONIZATION DATA FOR η^5-$C_5H_5Mn(CO)_2NH_3$

Peak	Ionization potential	Relative amplitude	W_h	W_l	Relative area
1	6.63	0.66	0.27	0.21	0.99
1'	6.99	1.00	0.45	0.42	
1'	7.36	0.81	0.37	0.21	
2	9.15	1.46	0.71	0.44	1.00

Discussion

The gross features of the ionization spectra of $CpMn(CO)_2N_2$ and $CpMn(CO)_2NH_3$ have been assigned by comparing them to the spectrum of $CpMn(CO)_3$. Thus, the ionizations occurring between 6.5 and 8.5 eV are ascribed to the three electron pairs primarily associated with the metal, and those between 9 and 10 eV are assigned to the two electron pairs associated predominantly with the ring e_1'' levels. The individual binding energy shifts of these bands have important implications to the interpretation of the structure of these complexes.

It must be emphasized that interpretations of photoelectron shifts based solely upon general band appearances and qualitatitive arguments are likely to be vastly incorrect. This point is exemplified quite well by the metal ionizations of $CpMn(CO)_3$ and $CpMn(CO)_2N_2$. For $CpMn(CO)_3$ the ionizations associated predominantly with the three occupied metal d levels may not be resolved into distinctly separate ionization bands, whereas for $CpMn(CO)_2N_2$ a single band is now observed at a lower binding energy than the other two. Because these three levels are principally involved in π-type interactions with the CO and N_2 ligands [12], a qualitative explanation of this order would suggest that N_2 is either a better π-acceptor or a poorer π-donor ligand than CO. Both of these suggestions are unreasonable in light of the known structures of N_2 and CO. It is apparent that a more sophisticated approach is required. The following discussion uses the methods developed during our previous investigation of the photoelectron spectra and the electronic structure of substituted η^5-cyclopentadienylmetal carbonyl complexes [12].

$CpMn(CO)_2N_2$

The electronic structure of $CpMn(CO)_2N_2$ was calculated according to the procedure outlined in the experimental section. From the measured ionization potentials of $CpMn(CO)_3$ and the calculated eigenvalues of $CpMn(CO)_3$ and $CpMn(CO)_2N_2$, it is possible to predict the ionization potentials of $CpMn(CO)_2N_2$. This prediction is made with the assumption that those factors which account for the difference between Koopmans' theorem [23] predicted ionization potentials and observed ionization potentials for a single molecule, such as relativistic effects, electron correlation, or electron reorientation in the positive ion [24], will be relatively constant for similar ionizations from two similar molecules. Thus, the scale factors determined from the orbital eigenvalues and observed ionization potentials of $CpMn(CO)_3$ may be used to adjust the calculated eigenvalues of $CpMn(CO)_2N_2$ for prediction of the experimental binding energies. These predictions are shown in Table 3. The predicted binding energies for $CpMn(CO)_2N_2$ are extremely close to the observed binding energies, suggesting that the individual electronic interactions are being weighed correctly. With this parameter-free model fortuitous agreement is highly unlikely.

The trends in these eigenvalues are clarified by the molecular orbital diagrams of $CpMn(CO)_3$ and $CpMn(CO)_2N_2$, as shown in Fig. 6. In this diagram, emphasis is placed on the relative interactions of the CO and N_2 ligands with the metal center. The orbitals of these groups are described in terms of the free ligand bases. This description is familiar for CO. The 5σ orbital of CO, which is primarily the carbon "lone pair" orbital, acts as a σ donor to the metal. The 2π orbital of CO, which is virtual in the free ligand and is localized mostly on the carbon, stabilizes the occupied metal levels by accepting electrons. As in the ab initio calculations [4], the orbital energies of the N_2 $3\sigma_g$ and $1\pi_g$ levels are similar to those of the CO 5σ and 2π levels. However, because N_2 is a homonuclear diatomic molecule, these orbitals are distributed equivalently on the two nitrogen centers. This spatial distribution reduces the overlap of these orbitals with the metal center, and hence decreases the metal—ligand interaction. The details of these considerations have been discussed previously [6].

The result of these different ligand—metal interactions is that the calculated eigenvalues of $CpMn(CO)_2N_2$ are slightly higher than those of $CpMn(CO)_3$. The primary factor causing this trend is the lower π-acceptor ability of the N_2 ligand ($0.441\ e^-$) compared to the CO ligand ($0.617\ e^-$) *. This decreased π-acceptance of the ligand results in less bonding stabilization of the metal levels and also a greater electron density at the metal center. The charge effects also influence the ionization of the ring e_1'' levels.

The increase in charge at the metal center is reduced somewhat by the slightly poorer σ donor ability of N_2 compared to CO. This is also a natural consequence

TABLE 3

KOOPMANS' THEOREM PREDICTION OF THE IONIZATION POTENIALS (eV) OF $CpMn(CO)_2N_2$ FROM APPROXIMATE CALCULATIONS AND $CpMn(CO)_3$ IONIZATION DATA

$CpMn(CO)_3$				$CpMn(CO)_2N_2$		
Predominant character	Eigenvalues	Experimental binding energy [12]	Correction	Eigenvalues	Predicted binding energy	Experimental binding energy
	−9.35	8.05	1.30	−8.80	7.50	7.54
Metal *d*	−9.35	8.05	1.30	−9.01 [a]	7.82	7.89
	−9.48	8.40	1.08	−9.26 [a]	8.07	8.07
Ring e_1''	−13.52	9.90	3.62	−13.38	9.76	9.78

[a] These levels are linear combinations of the corresponding levels of $CpMn(CO)_3$, and thus the corrections are averaged.

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* Standard Mulliken population analysis is used throughout.

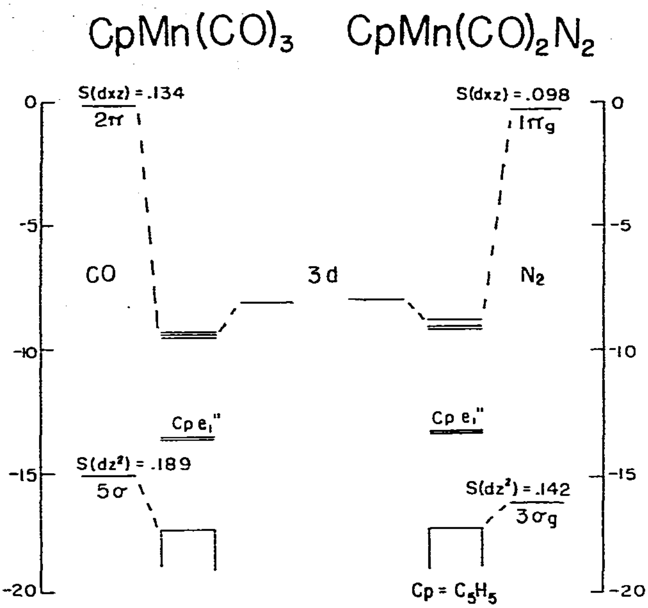

Fig. 6. Comparison of the molecular orbital diagrams of CpMn(CO)$_3$ and CpMn(CO)$_2$N$_2$. The overlaps of metal orbitals at the origin with ligand orbitals on the positive z axis are indicated.

of the charge distribution of the N$_2$ σ orbitals, and has been discussed previously [6]. The total σ donation of the N$_2$ group is calculated to be 0.497 e$^-$ compared to 0.583 e$^-$ for CO. The net changes in the electron distribution in the remainder of the molecule when CO is replaced by N$_2$ are quite small, which undoubtedly accounts for much of the difficulty in using other physical or chemical properties for comparing the bonding of CO and N$_2$. For instance, when one N$_2$ is substituted for one CO in the calculation on CpMn(CO)$_3$, the π-acceptor ability of the remaining carbonyls changes by only 0.003 e$^-$.

This description is significantly different from that of a recent SCCC-MO study of the same complexes [7]. Both studies conclude that N$_2$ is a poorer π-acceptor than CO. However, from the SCCC-MO study of the bonding of N$_2$, it was concluded that the σ donor ability of N$_2$ is not much different than that of CO. It should be pointed out that an error on the order of 0.1 e$^-$ in the charge distrubtion of our calculations would lead to an error on the order of 1 eV in the prediction of the experimental binding energies. Therefore changes in π-acceptor ability from CO to N$_2$ must be accurately balanced with the changes in σ donor ability to achieve good agreement between the predicted and observed energies, barring the remote possibility of fortuitous cancellation of errors. The dinitrogen ligand must be interpreted as a slightly poorer σ donor than the carbonyl ligand. A more important error in the SCCC-MO results concerns the interactions of the occupied π bonds of N$_2$ and CO with the metal center. The SCCC-MO calculations [7] indicate that N$_2$ is a better π-donor than CO. It is true that the 1π$_u$ orbitals of N$_2$ interact more strongly with the metal center than the 1π orbitals of CO, which are largely localized on the oxygen center. However, the 1π$_u$ and 1π orbitals of N$_2$ and CO are interacting with fully occupied metal levels. Thus these orbitals of N_2 and CO are not π-donors, but share the electron density with the occupied metal levels. These errors in the SCCC-MO method may be traced to particular approximations used in that method, as has been discussed previously [6].

$CpMn(CO)_2NH_3$

A comparison of the molecular orbital diagram of $CpMn(CO)_2NH_3$ with that of $CpMn(CO)_3$ is shown in Fig. 7. The NH_3 ligand is an interesting contrast to both the N_2 and CO ligands in that the NH_3 ligand has no readily available π-acceptor orbitals. The metal—amine bond is produced by a σ interaction of the metal levels with the $2a_1$ orbital of NH_3, which is the nitrogen "lone pair". This nitrogen "lone pair" acts as an electron donor to the metal system. The net effect of these interactions is that the eigenvalues in the calculation of $CpMn(CO)_2NH_3$ are significantly destabilized with respect to the eigenvalues of $CpMn(CO)_3$. Also, there is a greater separation in energy between the eigenvalues of the predominantly metal levels. These trends are observed in the comparison of the spectrum of $CpMn(CO)_2NH_3$ with the spectrum of $CpMn(CO)_3$.

As with the $CpMn(CO)_2N_2$ case, the ionization potentials of $CpMn(CO)_2NH_3$ may be predicted from the eigenvalues of the calculations on $CpMn(CO)_2NH_3$ and $CpMn(CO)_3$ and the observed ionization potentials of $CpMn(CO)_3$. These predictions are compared with the observed values in Table 4. The correlation of the predicted and experimental ionization potentials of $CpMn(CO)_2NH_3$ is not as successful as in the case of $CpMn(CO)_2N_2$. The predominantly metal ionizations are predicted to occur at a bonding energy from 0.55 to 0.95 eV lower than observed, and the predominantly ring e_1'' ionizations are predicted 0.26 eV

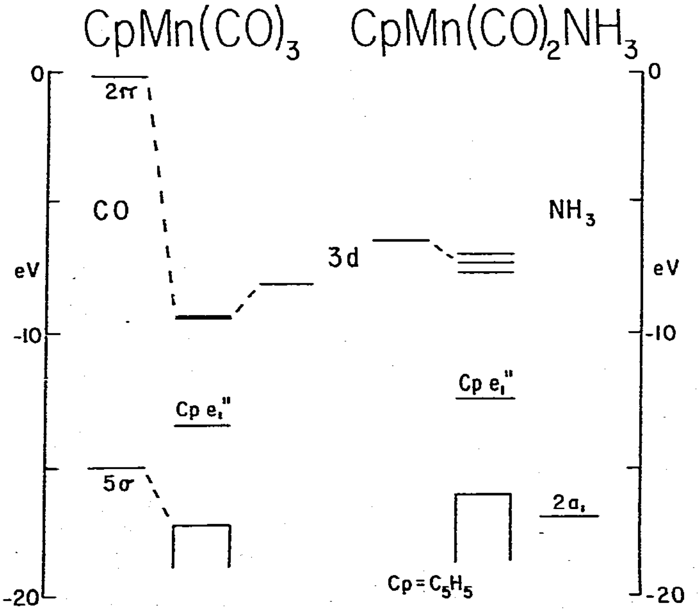

Fig. 7. Comparison of the molecular orbital diagrams of $CpMn(CO)_3$ and $CpMn(CO)_2NH_3$.

TABLE 4

KOOPMANS' THEOREM PREDICTION OF THE IONIZATION POTENTIALS (eV) OF $CpMn(CO)_2NH_3$ FROM APPROXIMATE CALCULATIONS AND $CpMn(CO)_3$ IONIZATION DATA (TABLE 3)

$CpMn(CO)_2NH_3$			
Eigenvalues	Predicted binding energy	Experimental binding energy	Error
−6.98	5.68	6.63	0.95
−7.29	6.10	6.99	0.89
−8.00	6.81	7.36	0.55
−12.51	8.89	9.15	0.26

too low. These discrepancies may be due to limitations in the approximate methods used. However, they may also be a result of attempting to use Koopmans' theorem to relate the eigenvalues of ground state calculations to ionization potentials. From comparison of a similar ab initio study on $Cr(CO)_6$ and $Cr(CO)_5$-NH_3, it appears that this latter situation is the most probable. The predicted ionization potentials from ab initio calculations on $Cr(CO)_6$ and $Cr(CO)_5NH_3$ and the observed ionization potential of $Cr(CO)_6$ are presented in Table 5. These ab initio calculations also indicate that the ionizations will occur at lower binding energy than is observed. The error for the metal ionizations is again 0.5 to 0.9 eV, the same error found from the approximate calculations. Thus, the approximate and ab initio methods both predict the same trends in ground state eigenvalues.

These results indicate that the approximate calculations account quite well for the ground state electronic structure and bonding of nitrogen complexes in comparison to the usual carbonyl situation. It is also evident from this work that special care must be exercised in deducing these quantities from any particular physical property of the complexes. In the case of photoelectron spectra, Koopmans' theorem may or may not be capable of accounting for trends in the ionization potentials. The theoretical calculations are helpful in sorting out which features of the ionization spectra are related to ground state properties.

TABLE 5

KOOPMANS' THEOREM PREDICTION OF THE IONIZATION POTENTIALS (eV) OF $Cr(CO)_5NH_3$ FROM AB INITIO CALCULATIONS [13] AND $Cr(CO)_6$ IONIZATION DATA

$Cr(CO)_6$			$Cr(CO)_5NH_3$			
Eigenvalues	Experimental binding energy	Correction	Eigenvalues	Predicted binding energy	Experimental binding energy	Error
−10.70	8.40	2.30	9.25	6.95	7.85	0.90
			9.33	7.03	7.56	0.53

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