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The Chemistry of Silica-Supported Chromium Ions: Calorimetric and Spectroscopic Study of Nitric Oxide Adsorption

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At the surface of CO-reduced, low-loaded (0.5% by weight) chromia/silica samples, four kinds of divalent Cr ions are present. All react with NO eventually yielding linear dinitrosyl species. Differences are found as to the energetic and kinetic behaviour. The most exposed ions (A and B) readily form dinitrosyls, with NO infrared stretching vibrations at 1747–1865 and 1755–1880 cm^{-1}, respectively. Less reactive Cr ions (designated C1 and C2) form at low coverage stable mononitrosyls (NO stretch at 1810–1815 cm^{-1}), which change at high NO pressure into A and B dinitrosyls (C1 ions) or to new dinitrosyls (C2 ions: NO stretches at 1765–1987 cm^{-1}). The different behaviour is explained assuming that A, B, and C ions are, before reaction, respectively 2-, 3-, and 4-coordinate to the surface.

INTRODUCTION

In a previous paper on the chemistry of silica-supported Cr ions (*1*), microcalorimetry and ultraviolet spectroscopy have been used to characterize low-loaded chromia/silica catalysts. It has been shown that, after careful reduction with CO, two kinds of exposed Cr ions (labelled Cr_A and Cr_B) and two types of less-exposed Cr ions (respectively Cr_{C1} and Cr_{C2}) are at the surface. On the former two, oxygen adsorption takes place at room temperature and occurs with comparable reaction heats. The oxidation of the latter two species only occurs at high temperature. Heating of the reduced sample at high temperature *in vacuo* or in reducing conditions (thermal deactivation) deactivates it, by converting Cr_A into Cr_C which is inactive towards oxygen, whereas Cr_B seems to be unaffected. Thus, the relative population of Cr_A and Cr_B may be calculated through the comparison of the extent of reoxidation at room temperature on active and deactivated samples. In this way Cr_A and Cr_B were estimated to be 45 and 25%, respectively, on the most active samples. The rest are C-type Cr ions. The reoxidation experiment at high temperature enables one to determine that the average oxidation number of Cr ions on the reduced sample is around 2.10. This means that the vast majority of Cr ions are in the divalent state. The systematic discrepancies from the ideal value of 2.00 may be interpreted in two different ways: (i) presence of some 10% of reactive Cr(III), which obviously requires less oxygen to reach the six-valent state, or (ii) presence of some 2% of Cr(III) clustered in α-chromia-like particles which are not reactive at all.

In a previous series of papers (*2–5*), some of us favored the former hypothesis. We now have evidence (some of which is collected in the Discussion) that the latter is the correct one.

To gain evidence about the coordinative state of surface Cr ions, we are examining the reactivity of reduced chromia/silica towards simple molecules. In the present paper, adsorption of nitric oxide is considered.

Several papers have already been devoted to this subject. To our knowledge,

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the first one is by Eley and co-workers (*6*) and goes back to 1973. In 1975, one of our two groups published a detailed infrared study (*4*), reporting the formation on Cr ions of dinitrosylic complexes. In the same year, three other papers appeared, one by Krauss and Weisser (*7*), reporting the same assignment, and two by Kugler *et al.* (*8, 9*), giving the surface species a rather different interpretation (complexes of the *cis*-dimer of NO).

Other investigations have since dealt with the stability of adsorbed NO (*10*), the high temperature reaction with CO (*10–12*), and the formation of mixed dinitrosylic complexes (*5, 13*) by further adsorption of other ligands. Quite recently, Beck and Lunsford (*14*) published an ESR and infrared study of NO adsorption on systems close to that studied in the present paper, reporting the formation of Cr(III) dinitrosyls visible in ESR.

Besides the problem of the valence state of Cr ions, the present work has two other relevant aspects. First, we shall advance further evidence in favour of the formation of dinitrosylic complexes. This is necessary, as some authors (*11, 12, 15*) are still uncertain about which model to favour. Secondly, there has been hitherto a lack of data concerning the energetics of NO adsorption and also its kinetics, and the present paper deals particularly with these. As in previous papers (*1–4*), we make systematic use of the thermal deactivation of the samples to discriminate between the behaviours of Cr_A, Cr_B, and Cr_C.

EXPERIMENTAL

Sample preparation, activation procedure, and thermal deactivation have been thoroughly described in Ref. (*1*), together with the experimental techniques. We briefly recall the following: (i) The adopted loading is about 0.5%, i.e., definitely lower than those of the industrial catalysts. (ii) The samples first undergo severe dehydration at 1023 K, then oxidation at 823 K under 40 Torr O_2 (1 Torr = 133 N m^{-2}), and are finally reduced at 623 K with 40 Torr CO for 30 min. This reduced *standard* sample is henceforth called an S sample. (iii) To deactivate the sample, it is kept at 973 K typically for 4 h *in vacuo*. The *deactivated* sample is called a D sample.

Reaction heats and related uptakes have been measured on a Tian–Calvet twin microcalorimeter kept at 310 K, by dosing very small amounts of gaseous NO (*1*). Diffuse reflectance spectra have been taken on a Beckman DK2 instrument. Spectra are shown in the following as $F(R_\infty)$ vs wavenumber, $F(R_\infty)$ being the Schuster–Kubelka–Munk function of the measured reflectance R_∞. Infrared measurements have been taken on a Beckman IR-7 double-beam spectrophotometer.

RESULTS

As the spectra of adsorbed NO show some dependence upon pressure and time of contact, we have chosen as standard conditions 1 Torr NO immediately after contact. This is illustrated in Fig. 1, both for samples S and D.

Section a in Fig. 1 shows the ir spectra in the region of nitrosyl stretching modes, no other signal appears elsewhere. The S spectrum coincides with those already published, both by some of us (*4*) and others (*7, 8*). It is dominated by two intense bands at 1747 and 1865 cm^{-1} assigned by us (*4*) and others (*7, 10*) to the out-of-phase and in-phase vibrations of a dinitrosylic complex $Cr^{II}(NO)_2$. Minor features are the slight asymmetry on the high frequency side of the band centered at 1865 cm^{-1} and the weak band at about 1810 cm^{-1}. Both these features are magnified by the deactivation process. In fact, the central band (now found at 1815 cm^{-1}) increases remarkably at the expense of the 1747–1865 cm^{-1} pair, whose decrease reveals a shoulder at 1880 cm^{-1} (responsible for the above quoted asymmetry) and a component at 1755 cm^{-1}. These latter constitute another kind of dinitrosylic complex, assigned in Ref. (*3*) to surface Cr(III). The central band

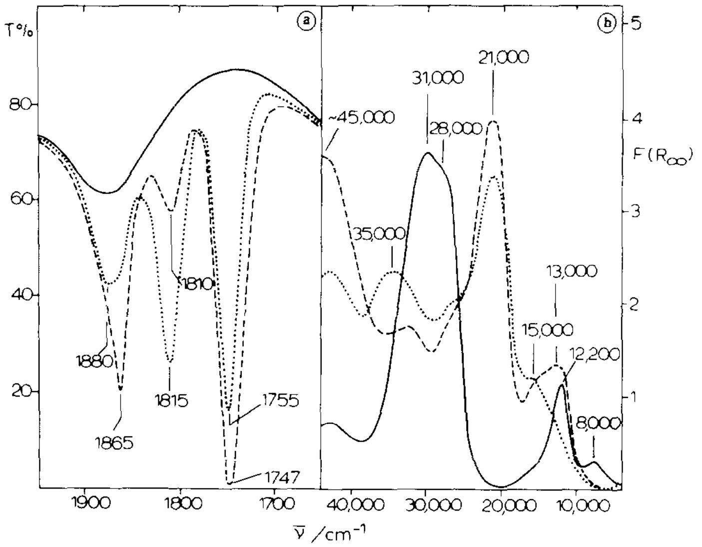


FIG. 1. NO adsorption in standard conditions. (a) ir spectra. Solid curve—background; dashed curve—S sample; dotted curve—D sample. (b) Diffuse reflectance spectra. Solid curve—S sample before adsorption; dashed curve—the same after NO contact; dotted curve—D sample after NO contact.

is easily assigned to the mononitrosyl complex $Cr^{II}(NO)$.

Section b of Fig. 1 shows the uv–vis diffuse reflectance (DR) spectra of samples S and D in the same conditions as section a. So as not to overcrowd the figure, the reflectance spectrum of sample D before NO contact has been omitted: this spectrum, however, is reported and discussed in Ref. (*1*), and is also shown in the present paper in Fig. 6b. The starting spectrum of the S sample shows *d–d* transitions at about 8000 and 12,000 cm^{-1} and a pair of intense charge transfers around 30,000 cm^{-1}. Upon NO adsorption, these latter are destroyed, and substituted by strong absorptions around 45,000 and 21,000 cm^{-1}. Meanwhile, in the *d–d* region, a complex absorption is seen, with components at about 13,000 and 15,000 cm^{-1}; the original 8000 cm^{-1} band has disappeared. The changes caused on the spectrum of the NO-covered sample by previous thermal deactivation are as follows. The low-lying component of the *d–d* transitions (13,000 cm^{-1}) disappears, whereas the other one is unaffected. Both the charge-transfer transitions at 45,000 and 21,000 cm^{-1} are decreased (the former to a larger extent), but there is an increase of a component at ~35,000 cm^{-1} already present (although weak and at lower frequencies) in the S spectrum.

To illustrate the kinetic aspects of NO adsorption, a D sample is more suitable, since although S samples show the same behavior they do so to a more limited extent. Figure 2 describes the time dependence of the adsorption of small doses of NO on such a sample. Section a shows the changes induced in the infrared spectrum by the adsorption of one intermediate dose: it is seen that the central band first increases, then decreases slowly while both the 1747–1865 and 1755–1880-cm^{-1} pairs grow. In section b the intensity of the central band has been plotted as absorbance (optical density) against time for four successive doses. It is seen that the first two doses cause an instantaneous increase in intensity followed by a slow decrease. In the other two doses, the increase in the first stage is slower and observable. This leads to a definite maximum in the third dose (to which section a refers).

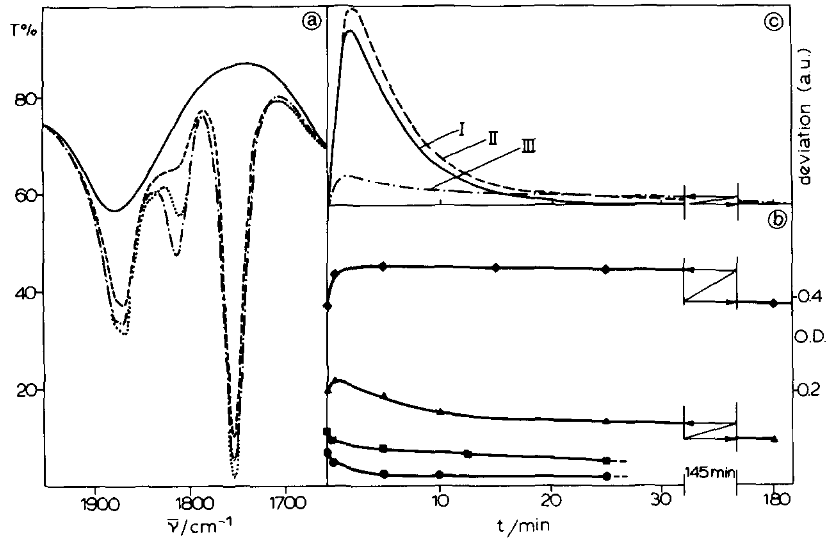


FIG. 2. Kinetic aspects of the adsorption of small doses of NO on D samples. (a) Changes in the ir spectra with time. Solid curve—background; dashed curve—starting spectrum (pseudoequilibrium pressure 1×10^{-3} Torr); dashed-dot curve—immediately after contact of 2.5×10^{-3} Torr NO; dotted curve—after 1 h. (b) Intensity of the 1810–1815-cm^{-1} band vs time for increasing doses (from ● to ◆). (c) Types of thermogram. Curve I: instantaneous process (small dose on an S sample). Curve II: slightly activated process (the same on a D sample). Curve III: very activated process (small dose on a D sample at high pressure).

Both the processes causing the increase and decrease of the central band slow down along the adsorption process, and the fraction of mononitrosyls reluctant to be transformed into dinitrosyls increases markedly as the pseudoequilibrium pressure increases.

Finally, section c of Fig. 2 reports the heat emission observed calorimetrically during the adsorption of doses on S and D samples. Three types of thermogram are shown. Type I coincides, within the instrumental sensitivity, with the heat emission expected for a quasi-instantaneous process. The slow processes occurring on sample D are revealed by the tail in type II, extending typically up to 200 min. Type III is a very activated adsorption encountered in different conditions to be described later.

Data in Fig. 2 show that, after some 30 min, the spectra vary little with time, but they do depend on the pseudoequilibrium pressure. To illustrate this fact, Fig. 3a reports the intensity in absorbance (OD) of the 1810–1815 and 1747 cm^{-1} bands (representative of mono and dinitrosyl species, respectively) as functions of the pressure. Pressures below 10^{-3} Torr were not investigated for instrumental reasons. S samples show an overwhelming intensity of the dinitrosyl species, which are very little pressure dependent, as they reach their maximum intensity within 0.01 Torr. The mononitrosyl species show a definitely larger pressure dependence, similar to that of the same mononitrosyl species on D samples. In both cases (although much less evident in the S case) the intensity of the 1810–1815 cm^{-1} band goes through a maximum around 1 Torr. Thereafter the decrease of the 1810–1815 cm^{-1} band is accompanied by a further increase of dinitrosyl species. This increase is not seen in the plot referring to the S sample, because the optical density of the 1747 cm^{-1} band is already exceedingly high. The increase in dinitrosyl intensity is actually related to a change in quality of the spectrum, illustrated by section b of the figure. Upon decrease of mononitrosyl species, the dini-

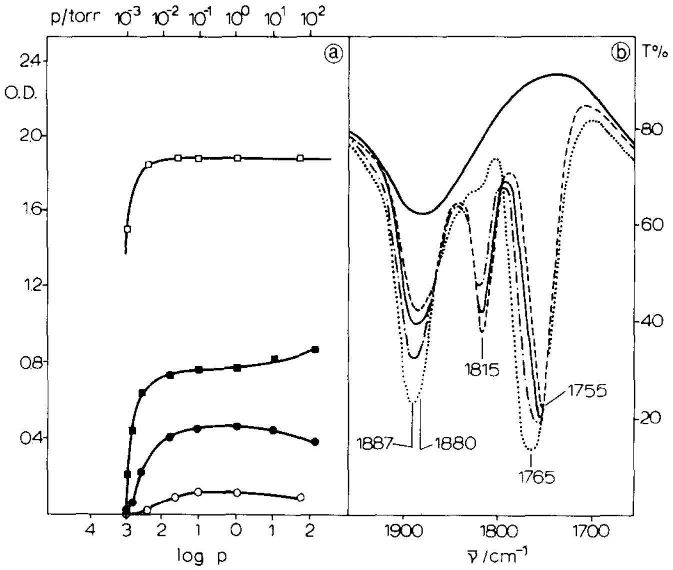


FIG. 3. Dependence of the ir spectrum of S and D samples upon the pseudoequilibrium pressure of NO. (a) intensity of the 1810–1815-cm^{-1} (circles) and 1747–1765-cm^{-1} (squares) bands against log p Open symbols—S samples; black symbols—D sample. (b) Spectra of a D sample at high NO pressures. Bold solid curve—background; dashed curve—1 Torr NO; thin solid curve—10 Torr; dashed-dot curve—120 Torr; dotted curve—120 Torr after 50 h.

trosyl bands grow shifting to higher frequency, because a new kind of dinitrosyl is formed at high pressure. This will be shown clearly later on, in a different experiment which enables the new absorptions to be precisely located at 1765 and 1887 cm^{-1}. When the sample is allowed to stand in NO atmosphere long enough (last curve in Fig. 3b), the 1815 cm^{-1} band is diminished and the dinitrosyls newly formed reach their maximum intensity.

Data in Fig. 3a are optical isotherms for the adsorption of NO on S and D samples. They can be usefully compared with similar volumetric and calorimetric data, which are shown in Fig. 4. In fact, in all cases results are taken some 30 min after NO contact. Here and in the following, terms like isotherms and pressure are used, notwithstanding the obvious fact that a true equilibrium is never attained.

As already shown in Fig. 3, NO uptake on both kinds of samples occurs first without a detectable pseudoequilibrium pressure (less than say 0.01 Torr), then adsorption becomes pressure dependent. On S samples, some 1.75 NO per Cr ion (0.55 μmol m^{-2}) is adsorbed in the former step, while only 0.16 NO/Cr (0.05 μmol m^{-2}) is adsorbed at pressures up to 10 Torr. The overall activity of a D sample is much less and quite different its pressure dependence: about 0.45 NO/Cr (0.14 μmol m^{-2}) are adsorbed below 0.01 Torr, some 0.30 NO/Cr (0.9 μmol m^{-2}) in the range 0.01–1 Torr, and further 0.09 NO/Cr (0.03 μmol m^{-2}) up to 10 Torr.

NO adsorbed under pressure is partially removable from the surface by expansion *in vacuo* and successive evacuation (desorption branches in Fig. 4). In the S case, the desorbed amount (as well as the released heat) roughly equals the amount adsorbed in the pressure dependent branch.

The corresponding desorption experiment in ir (not reported) shows that only the mononitrosyl species are desorbed, i.e., dinitrosyls on S samples are stable.

In the D case, only a fraction (some 18%) of the heat released in the pressure-dependent branch is recovered upon pumping. This means that irreversible processes have

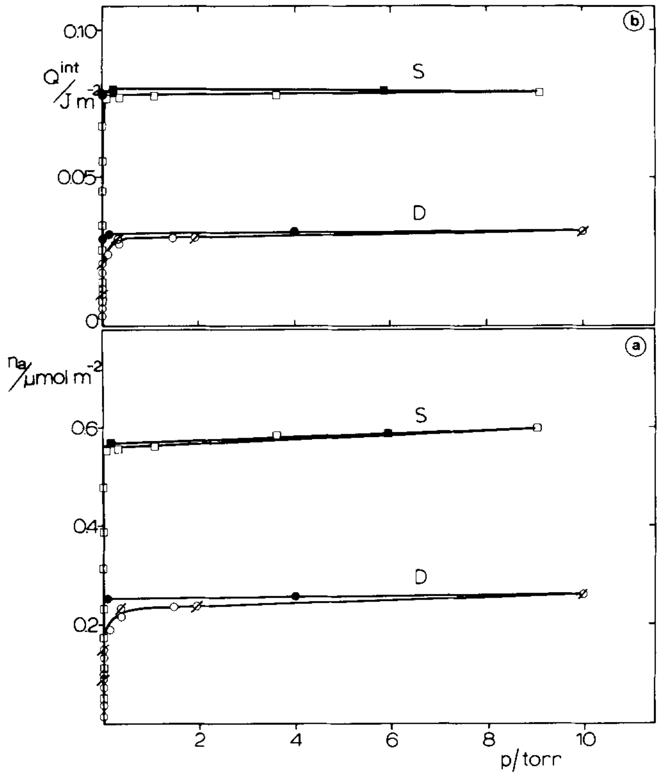


FIG. 4. Adsorption isotherms. (a) Volumetric data (amount adsorbed vs pressure). (b) Calorimetric data (integral heat vs pressure). Open symbols—adsorption; black symbols—desorption. Crossed symbols in the adsorption on D samples refer to different runs.

taken place under pressure in agreement with what is shown in Fig. 3b. Infrared desorption experiments (not reported) show that the heat recovered is due to the limited desorption of both mononitrosyls and newly formed dinitrosyls.

Heat emission in the S case is quick in the first stage (type I thermograms), and becomes suddenly activated when adsorption occurs under pressure (type III thermograms in Fig. 2c). On D samples, heat emission is at first nearly instantaneous, except for a long tail (type II), and gradually turns to the activated type III at high pressure.

Figure 5 reports emitted heats plotted against adsorbed amounts, for both S and D samples. In the former case (section a), the adsorption in the absence of pressure yields a constant molar heat of 138 kJ mol^{-1}, the rest of the adsorption process being characterized by a much lower adsorption heat. As to the D samples (section b) adsorption occurs in the whole range of pressure up to 1 Torr at 126 kJ mol^{-1}, i.e., quite energetically, although slightly less than in the previous case; above 1 Torr adsorption involves about 92 kJ mol^{-1}.

Finally, NO adsorption has been monitored on a D sample which first had been contacted with oxygen at room temperature. Under those circumstances, both A and B types of Cr have reacted (*1*) with molecular oxygen to form chromates (or possibly dichromates), and so the chemistry of C-type Cr ions toward NO should be singled out. Figure 6 describes such experiments. Section a of the figure shows the ir spectrum of the sample in the nitrosylic region. It is seen that below 1 Torr mononitrosyls are basically formed (band at 1815 cm^{-1}) together with small amounts of "regular" dinitrosyls, absorbing at 1747–1755

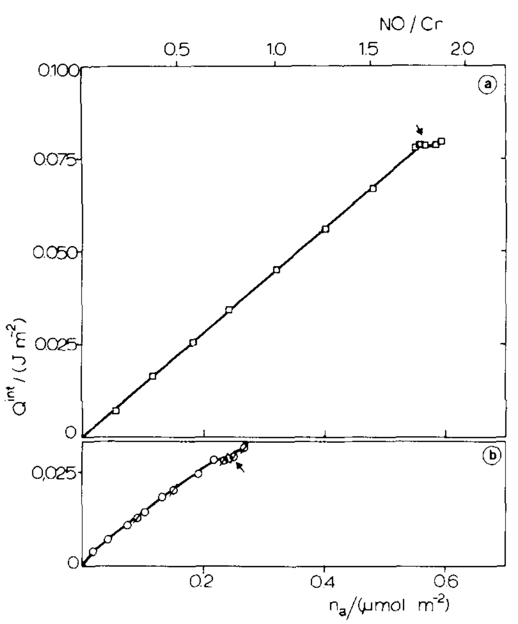


FIG. 5. Integral heats against adsorbed amounts. (a) S sample. (b) D sample. Arrows show the appearance of a pseudoequilibrium pressure around 1 Torr. Symbols as in Fig. 4.

and 1865–1880 cm^{-1}. At higher pressure and longer time of contact (dashed-dot curve), mononitrosyls are converted into a new type of dinitrosyl complexes that absorb at 1765 and 1887 cm^{-1}, and which now overwhelm the other kinds of bimolecular complexes.

The same experiment has been followed by microcalorimetry. Up to 0.1 Torr, thermograms are of type II and the mean molar heat is rather high, about 150 kJ mol^{-1}: about 0.20 NO/Cr adsorbs under those circumstances. At higher pressures, slow (type III) thermokinetics and lower heats (about 90 kJ mol^{-1}) are recorded. Section b of Fig. 6 illustrates the same experiment in uv–vis (up to 1 Torr). The solid curve is the DR spectrum of a D sample (already referred to), the dashed curve is the spectrum after O_2 chemisorption at room temperature and the dotted curve is taken after NO contact: the original *d–d* transitions have disappeared and a band at about 15,000 cm^{-1} is seen, as on the D sample which has not presorbed oxygen (dotted curve in Fig. 1b).

DISCUSSION

Mechanism of Adsorption

Quantitative data in Fig. 5 show that on an S sample, the vast majority of surface Cr

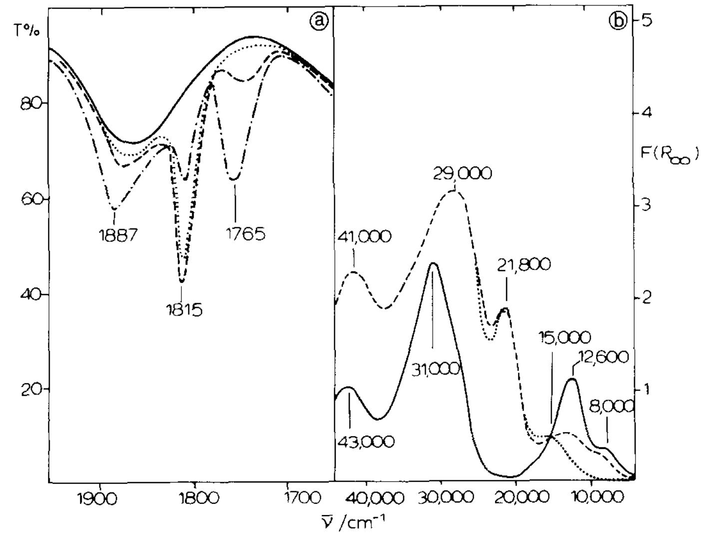


FIG. 6. NO adsorption on a D sample pretreated with 40 Torr O_2 at room temperature for a few minutes and evacuated. (a) ir spectra. Solid curve—background; dotted curve—0.1 Torr; dashed curve—1 Torr, after 30 min; dashed-dot curve—70 Torr after 90 min. (b) Diffuse reflectance spectra. Solid curve—before any reaction; broken curve—after contact with O_2; dotted curve—1 Torr NO.

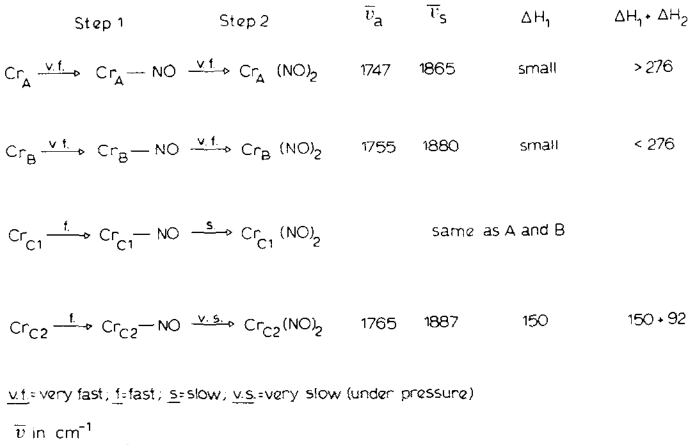
ions adsorb two NO molecules. The structure of these bimolecular complexes will be discussed in detail below. It is, however, evident that they give rise in the infrared to two modes. As shown in Ref. (*1*), thermal deactivation converts A-type chromium into C type, leaving B-type ions unaffected. Data in Fig. 1a thus suggest that the 1747–1865 cm^{-1} pair, which disappears upon thermal deactivation, has to be assigned to a couple of NO molecules adsorbed (no matter for the moment how) onto A-type ions. Similarly, the pair at about 1755–1880 cm^{-1} (basically unaffected by the thermal treatment) is ascribable to two NO molecules on B-type chromium.

The central band at 1810–1815 cm^{-1} is clearly due to a mononitrosyl complex surely involving C sites. However, the intensity changes in Fig. 2b and the variations in frequency with coverage show that its nature is composite. In fact, mononitrosyl complexes of all kinds of surface ions (i.e., A, B, C1, and C2) may contribute to it. To discriminate between the possible contributions, we make reference to the adsorption of NO on an oxygen-pretreated D sample (Fig. 6), as sites A and B have already reacted, and the sole reactivity of C1 and C2 is manifested. The first consideration is that indeed two different kinds of are less reactive Cr ions are involved in the adsorption of NO. One (say C1 for convenience) coordinates one NO molecule quite rapidly, followed by a second molecule in a process which is slow but not too activated, and which is responsible for the tail in the heat-emission peak of type II. The bimolecular complex arrived at is the same as those formed on A and B types of chromium. The second type of little-reactive Cr (say C2) only coordinates one NO in the absence of a substantial pressure. When the NO pressure is greater than 1 Torr, a very activated process (type III thermogram) leads to a bimolecular complex of a new type, absorbing at 1765 and 1887 cm^{-1}.

As C1 and C2 ions are obviously present on D samples which have not presorbed oxygen, similar features are observed for NO adsorption on such samples. At low coverages in the absence of a substantial NO pressure, heat is emitted by a type II thermokinetics (Fig. 2c). The behavior with time of the 1810–1815 cm^{-1} band, shown in Fig. 2b, can be interpreted as the superposition of two different mononitrosyls, one involving C1 sites (first increasing, then decreasing with time), the other involving C2 Cr ions, whose intensity steadily increases with the pseudoequilibrium pressure. At pressures higher than 1 Torr, C2 mononitrosyls react to give the new type of bimolecular complexes (Fig. 3), and the thermokinetics are of type III.

Although much less evident, the reactivity toward NO of C1 and C2 Cr ions can be observed also on S samples. Upon adsorption of a small NO dose, the intensity of the 1810 cm^{-1} band goes through a maximum: when the NO pressure is higher than 1 Torr, heat-emission kinetics suddenly change and lower molar heats are recorded (last portion of the plot in Fig. 5a). There are probably some differences in the energetics of the C-type Cr ions on D and S samples. The last portions of the plots in Fig. 5 (pseudopressure above 1 Torr) show a smaller slope (molar heat) in the S case: accordingly, the species formed under pressure are observed to be readily desorbable on S samples only. Apart from these minor features, NO adsorption on S samples is an instantaneous phenomenon (type I thermograms): this means that basically both steps of NO coordination onto A and B Cr ions are nonactivated, in agreement with what has already been found for oxygen chemisorption.

The mechanism of adsorption and its kinetic features are summarized in Scheme 1. It must be stressed that this scheme is probably an oversimplification: types of Cr ions are likely to be families of like species (as already pointed out by oxygen adsorption (*1*)), so that the behaviors of different species have to be considered average ones (*16*).



Step 1	Step 2	$\bar{\nu}_a$	$\bar{\nu}_s$	ΔH_1	$\Delta H_1 + \Delta H_2$
$Cr_A \xrightarrow{v.f.} Cr_A{-}NO$	$\xrightarrow{v.f.} Cr_A(NO)_2$	1747	1865	small	>276
$Cr_B \xrightarrow{v.f.} Cr_B{-}NO$	$\xrightarrow{v.f.} Cr_B(NO)_2$	1755	1880	small	<276
$Cr_{C1} \xrightarrow{f.} Cr_{C1}{-}NO$	$\xrightarrow{s.} Cr_{C1}(NO)_2$	same as A and B			
$Cr_{C2} \xrightarrow{f.} Cr_{C2}{-}NO$	$\xrightarrow{v.s.} Cr_{C2}(NO)_2$	1765	1887	150	150 + 92

v.f.=very fast; f.=fast; s=slow; v.s.=very slow (under pressure)

$\bar{\nu}$ in cm^{-1}

ΔH in $kJmol^{-1}$

SCHEME 1

Energetics of Adsorption

Due to its complexity, it is not possible to characterize all steps in the adsorption mechanism from the energetic point of view. The conversion of A-type into C-type chromium caused by thermal treatment does not simplify the situation as C Cr ions still react with NO in an even more complicated manner, and, in particular, the conversion does not allow the discrimination of the processes on A and B sites, unlike the O_2 case (*1*). Thus, only an average value for the heat of formation of dinitrosyl complexes onto A and B sites can be given, namely 2 × 138 kJ/mol NO or 276 kJ/mol Cr. Some difference in energy is, however, expected between the two kinds of dinitrosyl because: (i) the different stability of A and B ions towards thermal deactivation, and (ii) NO is desorbed at 373 K from B sites only, whereas NO desorption from A sites starts some 100 K higher.

The difference, however, cannot be large. In fact, the infrared spectra of S samples at increasing NO coverages reported in detail in Ref. (*4*) show that bimolecular complexes on A and B ions are formed at a constant ratio, as the bands around 1865 cm^{-1} (comprehensive for the absorption of A and B-type complexes) has a constant shape. Indeed, were the energy of formation of bimolecular complexes onto A and B sites substantially different, a linear plot such as that in Fig. 5a would not be obtained, as the more energetic complexes would be formed first.

No energetic data are available on the first step of reaction (coordination of one molecule) onto A and B sites. It seems, however, that the first NO to be bound is held rather loosely. If the heat of adsorption of the first NO ligand were comparable with the mean value for the two ligands (i.e., 138 kJ mol^{-1}), the relative population of bi and monomolecular complexes would simply be given by statistical (entropic) factors of the type x^2 and $2x(1 - x)$, respectively (x = coverage), and a completely different trend with coverage would be observed. The evidence (small intensity of the 1810-cm^{-1} band, almost entirely ascribable to C ions) seems to be in favor of a heat of adsorption of the first NO negligible (on S sample) with respect to 138 kJ mol^{-1}.

Coordination of one NO ligand on C ions seems, on the contrary, to be highly energetic. Infrared data in Fig. 6a show that on oxygen-pretreated D samples the first step of adsorption basically yields mononitrosyls, and the corresponding differential heat is about 150 kJ mol^{-1}.

The same C sites are present on D samples which have not preadsorbed oxygen, but the adsorption is now comprehensive for the formation of mononitrosyls onto C2 sites and of bimolecular complexes onto C1 and B ions. As the slope of the diagram in Fig. 5b yields a mean molar heat for the two processes (126 kJ mol^{-1}) quite close to that (138 kJ mol^{-1}) of the corresponding diagram for an S sample (Fig. 5a), it is inferred that mononitrosyls on C2 ions are formed with a heat comparable to one-half of the heat of formation of dinitrosyls. In fact ir desorption experiments (not reported) show that C2 mononitrosyls are very little desorbed at RT thus showing a stability close to that of dinitrosyls.

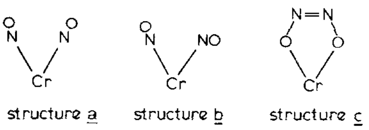
Lastly, we note that coordination of the second NO molecule on C2 sites involves a rather low heat of reaction (92 kJ mol^{-1}), as though to counterbalance the high energy of the first step of reaction.

A possible explanation for the low heat released in the second step, also accounting for its activated nature is that a ligand displacement reaction occurs involving the detachment of at least one oxygen surface ligand.

Thus the formation of dinitrosyls onto C2 ions seems to involve some (150 + 92) = 240 kJ mol^{-1} Cr, i.e., slightly less than 276 kJ mol^{-1} Cr, in agreement with their partial desorbability already at room temperature. In conclusion, the stability of dinitrosyls decreases along the series A, B, C2.

Structure of Adsorbed Species

The most straightforward hypothesis is that real *cis*-dinitrosyls are formed (structure a illustrated below) analogous to those well known in inorganic chemistry. The two observed bands are, in this hypothesis, the symmetric and antisymmetric stretching modes. A pair of bands in this spectral range could also be accounted for by structure b, with two nonequivalent (and therefore little coupled) NO vibrators, one of which is partially bent (*17*). Isotopic substitution experiments by Kugler and Gryder (*9*) show, however, that the two NO oscillators are equivalent. The ratio between the intensities of asymmetric and symmetric modes (I_a/I_s) furnishes, on the basis of simple vectorial model, the angle between the oscillators (*18*). The observed ratio 3.79 (*4*) is rather high and yields a figure about 120°. This has led Kugler and Gryder (*9*) to reject the simple model of *cis*-dinitrosyls, and to invoke a different structure c, i.e., a complex of a *cis*-dimer of NO. As a matter of fact, the matrix-isolated *cis*-dimer of NO has two modes at 1862 and 1768 cm^{-1}, the former being about four times less intense than the latter (*19*).



SCHEME 2

The point, however, is that *cis*-dinitrosyls in tetrahedral complexes (*20*) can form an angle as large as 118°. It is thus unsafe to rely on this evidence alone for the refusal of structure a. Furthermore, dimers of NO have indeed been found at the surface whenever physisorption processes are concerned (alkali halides (*21*), silica and zeolites (*22*)). It seems on the contrary unlikely that such NO dimers could be invoked in a chemisorption process. In fact (i) no analogs of structure c exist in homogeneous complexes; and (ii) should the *cis*-dimer moiety ever bind to a Cr_A ion as in structure c, the N–O bond order would drastically change, and so would the stretching frequencies.

The 1747–1865 cm^{-1} pair is the only case among bimolecular complexes formed on surface Cr ions to show an abnormally high I_a/I_s. The other two pairs of bands related to dinitrosyls (1753–1880 and 1765–1887 cm^{-1}) have I_a/I_s definitely smaller, although a precise figure cannot be safely stated because of the strong overlap. Similarly, complexes of the type $Cr(NO)_2L$ formed on A sites by further adsorption of some molecules (*10, 11*) show I_a/I_s approaching unity. In particular, the complex $Cr(NO)_2CO$ has a ratio close to unity: the heat of adsorption of CO onto preformed dinitrosyl complexes is only 21 kJ mol^{-1} (*23*), so suggesting that no drastic change in structure occurs upon CO adsorption.

For all these reasons, we propose for all kinds of bimolecular complexes, including those formed on A sites, a structure like the one in a.

Valence State of Cr Ions

The stretching frequencies of the different dinitrosyls increase in the series A, B, and C2. This is best shown by the mean stretching frequency, which is 1806, 1817, and 1826 cm^{-1}, respectively. Such a fact is usually assumed to mean that the charge of the central ion is increasing along the series. This assumption seems to be in conflict with the evidence that Cr ions are divalent (*1, 7*) on carefully reduced samples. As a matter of fact, Beck and Lunsford (*14*) have found that the ESR-active Cr(III) dinitrosyls do absorb at 1753 and 1880 cm^{-1}, i.e., at the same frequencies as B-type dinitrosyls. However, they have also shown that after some 30 min of reduction in CO atmosphere, the Cr(III) concentration drops to a meager 4%, i.e., to a much lesser extent than B ions (some 25%). We thus assume that, although Cr(III) may be present as a minor feature and give rise to dinitrosyls with the same frequencies as those of B ions, the latter are not trivalent. Other pieces of evidence are as follows. If B ions were trivalent: (i) the average oxidation number would be 2.25, i.e., definitely higher than is measured; (ii) one ought to assign an even higher oxidation number (e.g., 4) to C2 ions causing the absorption at 1765–1887 cm^{-1}. This is quite unrealistic, unless NO itself had oxidized C2 ions. This does not happen below about 300 K (*4, 14*). Moreover, we have independent evidence that the apparently high charge of C2 ions is an intrinsic property, as CO adsorbs at low temperature on these ions with a high stretching frequency. A possible way to reconcile the conflicting evidence is to assume that the *actual* charge depends upon the number of oxygen ligands in the coordination sphere of Cr ions all *formally* divalent. Recent ESCA measurements on systems very close to those investigated by us (*24*) support the idea that oxygen ligands at the surface act as strong electron acceptors. Following this idea, it is tempting to assume for A, B, and C2 ions two, three, and four oxygen ligands, respectively. This could explain why up to three dinitrosyl species are observed, whose coordinative situation would respectively be tetrahedral (A-type dinitrosyls), incomplete (B type), and complete octahedral (C2 type). The angle between NO oscillators would decrease from about 120 to about 90°: the I_a/I_s ratio is thus expected, within the limits of the vectorial model, to decrease from 3.79 to 1. This is what is qualitatively observed in Figs. 1a and 3b. Moreover, whereas A and B types of dinitrosyl still possess coordinative vacancies and can thus bind further ligands, as shown in (*5*), C2 dinitrosyls should only give rise to ligand displacement reactions. Preliminary experiments show that this is so.

Electron Transitions of the NO-treated Samples

The question now arises whether all the species identified so far in the ir spectra, namely dinitrosyls on A, B, and C2 sites and mononitrosyls, also show up in the uv–vis spectra. Such measurements have all been run at low pressure, so that no data are available about dinitrosyls on C2 sites. Both Figs. 1b and 6b show that NO adsorption causes some changes below 20,000 cm^{-1}, i.e., in the *d–d* region of divalent chromium. The surface NO complexes still show *d–d* transitions, in particular two absorptions are seen at about 15,000 and 13,000 cm^{-1}. The comparison between S and D samples after NO contact (Fig. 1b) shows that the latter component is depleted by a previous thermal treatment. This allows the 13,000 cm^{-1} band to be assigned to dinitrosyl complexes on A sites. Simultaneously, the other component, which is the only one left, increases in intensity. Bearing in mind that B-type dinitrosyls and mononitrosyls predominate on this kind of surface, it is inferred that both species contribute to this absorption. Further evidence is given by Fig. 6b. Under the adopted conditions, mononitrosyls are predominantly formed (Fig. 6a), which cause the band at about 15,000 cm^{-1} but at a lower intensity. The position of the *d–d* bands of the surface complexes seems to depend on the coordination number of the central ion, which is, in our hypothesis, *4* for Cr_A (two oxygen and two NO ligands) and *5* for Cr_B and Cr_{C2} (three oxygen, two NO, four oxygen, and one NO ligand, respectively).

As to the charge-transfer region, it is observed that the thermal deactivation causes a decrease of the band around 45,000 cm^{-1} and the appearance of an absorption at about 35,000 cm^{-1}. Accordingly, we assign the former to A-type dinitrosyls, and the latter to mononitrosyls. B-Type dinitrosyls probably contribute to the 45,000-cm^{-1} band, as its intensity is far from being depleted by the thermal treatment. The 35,000-cm^{-1} band is not seen in Fig. 6b, probably because the spectrum is already quite intense at this frequency.

The band at 21,000 cm^{-1} is a peculiar feature of the spectrum. It is not present in Fig. 6b, i.e., it is related to dinitrosyls only. Its decrease upon thermal deactivation (Fig. 1b) further supports this idea. Its nature is puzzling as the frequency is exceptionally low for a charge transfer and its intensity is too high for a *d–d* transition.

As far as we are aware, the electronic spectra of dinitrosyls have never been discussed. A qualitative comparison may be made with inorganic complexes composed of ligands with a similar electronic structure, namely CN^- and O_2^-, which differ from NO by one and two electrons, respectively. In both cases, low energy CT absorptions are observed, of the type metal to ligand in the O_2^- case (*25*) and the reverse in the CN^- case (*26*). These bands, however, are not very intense, in contrast to what is observed in Fig. 1b for the 21,000 cm^{-1} band. A possible way to account for its features is to assume that there is extensive mixing of the metal and ligand wave functions (*26*). If so, a valid description can only be given in terms of molecular orbital theory, as is the case with oxyanions (e.g., CrO_4^{2-}), which indeed show bands similar to the one at 21,000 cm^{-1}.

CONCLUSIONS

Although probably better thought of as families of like ions rather than clear-cut individual species, the four kinds of divalent ion present at the surface of thoroughly reduced CrO_3/SiO_2 systems show distinct behaviors toward NO adsorption.

A-Type Ions

These form the majority on standard samples (about 45%), and are unstable toward thermal treatment, probably because they are bound to only two oxygen surface atoms. The coordination of a first NO ligand is fast and most probably slightly energetic, so that the immediate coordination of a second NO leads to a dinitrosyl surface complex of probable tetrahedral stereochemistry with NO stretching modes at 1747 and 1865 cm^{-1}, whose intensity ratio is about 3.79. On the basis of the vectorial model the angle between the oscillators is computed to be 120°. A strong synergic effect between the two NO ligands is observed. Although a precise figure cannot be stated, because NO adsorption on A and B sites occurs simultaneously, the formation of A-type dinitrosyls involves a heat of adsorption of at least $2 \times 138 = 276$ kJ per mol of the complex. Absorptions in uv–vis related to these dinitrosyls are at 13,000, 21,000, and 45,000 cm^{-1}, respectively, *d–d* and low and high-lying CT transitions. The position and intensity of the second band seem to indicate an extensive mixing between orbitals of the ion and the ligands, in agreement with the synergic effect referred to above. The low coordination number of

Cr_A, even after NO adsorption, is confirmed by the possible further insertion of ligands (*5*).

B-Type Ions

These are present as some 25% of the total Cr loading and are little affected by thermal treatments, probably because they are coordinated to three oxygen atoms of the surface. The formation of dinitrosyls on B sites is similar to that on A sites (see Scheme 1), i.e., the mononitrosyl is unstable and the rapid coordination of a second NO takes place. The overall process is likely to involve slightly less heat than in the A-type case. The corresponding stretching frequencies fall at 1755 and 1880 cm^{-1}: the increase in frequency is likely to mean that the actual charge of the central ion has increased with respect to A-type ions. Ultraviolet–visible absorptions related to B-type dinitrosyls are at 15,000, 21,000, and 45,000 cm^{-1}, again assigned as *d–d* and two CT transitions, respectively.

C1-Type Ions

These are little reactive and are more abundant on deactivated samples. They coordinate at a considerable (although observable) rate a first NO ligand (band at 1810–1815 cm^{-1}) and then a second one, giving rise to A and B types of dinitrosyl, in contrast with C2 ions which give rise to a new kind of dinitrosyl. In other words, the "shielding" process caused by the thermal treatment is, for these ions only, reversed by NO adsorption, which somehow extracts these ions from the oxidic matrix, as also does molecular oxygen very slowly at room temperature.

C2-Type Ions

These are very little reactive, are abundant on D samples, and are probably bound to four oxygen atoms of the surface. They coordinate rather slowly, but energetically, a first NO ligand (stretching mode at 1810–1815 cm^{-1}) below 1 Torr: the corresponding uv–vis absorptions are at 35,000 and 15,000 cm^{-1}, respectively, a CT and a *d–d* transition. At higher pressures, a second NO ligand is coordinated, with the release of about 92 kJ per mol of NO. The dinitrosyls that result absorb at 1765 and 1880 cm^{-1}, thus showing a rather high actual charge of the central ion.

REFERENCES

1. Fubini, B., Ghiotti, G., Stradella, L., Garrone, E., and Morterra, C., *J. Catal.* **66,** 200 (1980).

2. Zecchina, A., Garrone, E., Ghiotti, G., Morterra, C., and Borello, E., *J. Phys. Chem.* **79,** 966 (1975).

3. Zecchina, A., Garrone, E., Ghiotti, G., and Coluccia, S., *J. Phys. Chem.* **79,** 972 (1975).

4. Zecchina, A., Garrone, E., Morterra, C., and Coluccia, S., *J. Phys. Chem.* **79,** 978 (1975).

5. Garrone, E., Ghiotti, G., Coluccia, S., and Zecchina, A., *J. Phys. chem.* **79,** 984 (1975).

6. Eley, D. D., Rochester, C. H., and Scurrell, M. S., *J. Chem. Soc. Faraday Trans 1* **69,** 660 (1973).

7. Krauss, H. L., and Weisser, B., *Z. Anorg. Allg. Chem.* **412,** 82 (1975).

8. Kugler, E. L., Kokes, R. J., and Gryder, J. W., *J. Catal.* **36,** 142 (1975).

9. Kugler, E. L., and Gryder, J. W., *J. Catal.* **36,** 152 (1975).

10. Rebenstorf, B., Larsson, L., and Larsson, R., *Acta Chem. Scand.* **A31,** 877 (1977).

11. Shih, S. S., Shihabi, D. S., and Squires, R. G., "Proceedings, International Congress on Catalysis, 6th (London 1976)," p. 978. Chemical Society, London, 1977.

12. Raskó, J., and Solymosi, F., *J. Chem. Soc. Faraday Trans. 1* **76,** 2383 (1980).

13. Zecchina, A., Garrone, E., Ghiotti, G., and Borello, E., *in* "Catalysis: Homogeneous and Heterogeneous" (B. Delmon, and G. Jannes, Eds.), p. 243. Elsevier, Amsterdam/New York, 1975.

14. Beck, D. D., and Lunsford, J. H., *J. Catal.* **68,** 121 (1981).

15. Kazusaka, A., and Howe, R. F., *J. Catal.* **63,** 447 (1980).

16. Krauss, H. L., Rebenstorf, B., and Westphal, U., *Z. Anorg. Allg. Chem.* **414,** 97 (1975).

17. Pierpont, C. G., Van Derveer, D. G., Durland, W., Eisenberg, R., *J. Amer. Chem. Soc.* **92,** 4760 (1970).

18. Beck, W., Melnikoff, A., and Stahl, R., *Chem. Ber.* **99,** 3721 (1966).

19. Fateley, W. G., Bent, H. A., and Crawford, B., *J. Chem. Phys.* **31,** 204 (1959).

20. Johnson, B. F. G., and McCleverty, J. A., *Progr. Inorg. Chem.* **7,** 277 (1966); Dahl, L. F., deGil, E.

R., and Feltham, R. D., *J. Amer. Chem. Soc.* **91,** 1653 (1969); Strouse, C. E., and Swanson, B. I., *Chem. Commun.* 55 (1971).

21. Lubetzsky, A., and Folman, M., *Trans. Faraday Soc.* **67,** 3110 (1971); Woodward, A. J., and Jonathan, N., *J. Phys. Chem.* **75,** 2930 (1971).

22. Chao, Cheng-Chung, and Lunsford, J. H., *J. Amer. Chem. Soc.* **93,** 6794 (1971).

23. Garrone, E., Ghiotti, G., Giamello, E., and Fubini, B., *J. Chem. Soc. Faraday Trans. 1* **77,** 2613 (1981).

24. Strutz, J., Dissertation, Freie Universität, Berlin (1979); (Professor H. L. Krauss, private communication).

25. Miskowski, V. M., Robbins, J. L., Trettel, J. M., and Gray, H. B., *Inorg. Chem.* **14,** 2318 (1975).

26. Figgis, B. N., "Introduction to Ligand Fields," p. 247. Interscience, New York, 1957.