

740. *Charge-transfer Spectra of Some Inorganic Complexes in Solution.*

By J. C. BARNES and P. DAY.

The wavenumbers of charge-transfer bands in 1 : 1 complexes between an oxidizing metal and a series of reducing ligands are plotted against those for other metals with the same ligands. The resulting straight line plots are used to discuss the stereochemistry of copper, redox potentials, the spectra of thiocyanate complexes, and solvent effects.

SOLUTIONS of reducible metal ions and oxidizable anions frequently exhibit absorption bands in the visible and near ultraviolet regions which are commonly assigned to electron transfer from the anion to the metal. The absorption energy is also related to the electron-donating and -withdrawing power of the ions as measured by other parameters such as redox potentials and electronegativities. For example, Jørgensen¹ compared the energies of corresponding bands in the spectra of many hexahalides of second- and third-row transition metals. He found that the energy gaps between chloride and bromide, and bromide and iodide, remained constant throughout and that they were proportional to the Pauling electronegativity differences between the pairs of halogens. By considering the bands of different metals with the same halogen he was also able to obtain a set of "optical" electronegativities for the metals on the assumption that the observed electron-transfer energy was proportional to the difference between two energy terms, one characteristic of the metal and the other of the halogen.

Hexahalide complexes containing low-energy electron-transfer bands are not, however, available outside the second and third transition series, though Jørgensen has used tetrahalides and halogenopentammines in an attempt to set up a corresponding series of optical electronegativities for the first transition series.²

To calculate additive "optical" electronegativities the observed charge-transfer-energies must be corrected for the spin-pairing energy in the metal ion. The Racah inter electronic repulsion parameters B and E_3 and the ligand field splitting Δ which are needed to derive this energy are often difficult to estimate with sufficient accuracy. Frequently the spin-pairing energy term is large compared with the observed wavenumber and the uncertainty introduced limits the sensitivity of the optical electronegativity.

A major difficulty in extending this type of correlation to other parts of the Periodic Table is that the association constants for halide complexes are not large and decrease sharply with decreasing halogen electronegativity. That is to say, the lanthanides, actinides and first transition series belong to the Chatt-Ahrland A group. Thus, we cannot obtain spectra of aqueous solutions of species where the inner co-ordination shell is occupied entirely by halogen atoms and if we are to extend this type of correlation we must find another system.

One possibility is to use non-aqueous solvents of low dielectric constant. Thus, bands have been observed for bromide complexes of the reducible lanthanides in ethanol, though such complexes are never observed in dilute aqueous solution.³ An alternative is to consider species $M(H_2O)_{n-1}X$ where n is the favoured co-ordination in aqueous solutions, choosing anions X which give sufficiently stable complexes of this stoichiometry in aqueous solution.

Elsewhere we have reported formation constants and spectra of some complexes with the reducible trivalent lanthanides.⁴ These show that in dilute solution the only species that need be postulated is $M(H_2O)_{n-1}X$ if X is a weakly complexing ligand, such as thiocyanate or sulphate. The choice is limited to relatively highly reducing or extremely colourless

¹ Jørgensen, *Mol. Phys.*, 1959, **2**, 309.

² Jørgensen, *Mol. Phys.*, 1963, **6**, 43.

³ Jørgensen, *Mol. Phys.*, 1962, **5**, 271.

⁴ Barnes, preceding Paper.

anions since the bands appear well into the u.v. region and are of quite low intensity (ϵ 50—100).

The band positions (in kK) obtained for the suspected electron-transfer bands in the lanthanide complexes can be compared with data for analogous transition metal and actinide complexes. Some data exist for the well characterized species $\text{Cu}^{\text{II}}(\text{H}_2\text{O})_5\text{X}$, $\text{Fe}^{\text{III}}(\text{H}_2\text{O})_5\text{X}$, and $\text{UO}_2^{2+}(\text{H}_2\text{O})_{n-1}\text{X}$, but the best example of the formula type MY_{n-1}X is the set of complexes $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}$. Because of the high electronegativity of ammonia relative to X, the lowest energy intense u.v. bands have been repeatedly assigned to charge transfer from X to the cobalt atom. These cobalt pentammine bands are therefore a suitable background against which to study the dependence on X of the $\text{M}(\text{H}_2\text{O})_{n-1}\text{X}$ spectra. To avoid the uncertainty of the optical electronegativity method we have chosen to plot observed band energies without assuming any theoretical model.

Fig. 1 shows the positions of the first intense bands in $\text{Eu}(\text{H}_2\text{O})_{n-1}\text{X}$, $\text{Yb}(\text{H}_2\text{O})_{n-1}\text{X}$, $\text{Cu}(\text{H}_2\text{O})_5\text{X}$, $\text{Fe}(\text{H}_2\text{O})_5\text{X}$, and $\text{UO}_2(\text{H}_2\text{O})_{n-1}\text{X}$ plotted against the charge-transfer energies in $\text{Co}(\text{NH}_3)_5\text{X}$ for a series of ligands X. All spectra were measured in water except for the lanthanide halides which refer to uncharacterized species in ethanol (see below). The near 1:1 correlation observed in all the plots justifies our assumption that in the two

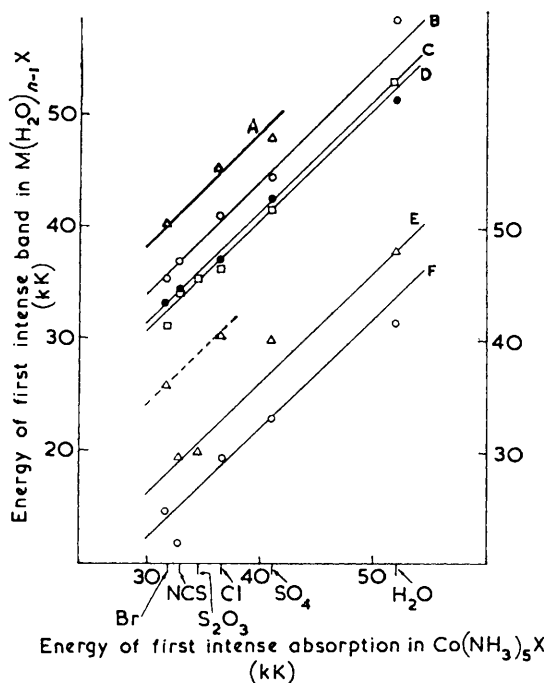


FIG. 1. The sources of the data are: FeNCS^{2+} , Perrin, *J. Amer. Chem. Soc.*, 1958, **80**, 3852; FeBr^{2+} , Lister and Rivington, *Canad. J. Chem.*, 1955, **33**, 1603; FeCl^{2+} and $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, Gamlen and Jordon, *J.*, 1953, 1437; FeSO_4^{+} , Whiteker and Davidson, *J. Amer. Chem. Soc.*, 1953, **75**, 3081; CuCl^{+} , McConnell and Davidson, *ibid.*, 1950, **72**, 3164; CuBr^{+} , Farrington, *ibid.*, 1952, **74**, 966; UO_2SO_4 , Morgans, Ph.D. Thesis, Univ. of Wales, 1959. Cobalt pentammine spectra are from von Kiss and Czegledy, *Z. anorg. Chem.*, 1938, **235**, 407. All the lanthanide data are from the preceding paper. Other points not referenced were measured during this study. A, Sm^{3+} ; B, Yb^{3+} ; C, UO_2^{2+} ; D, Eu^{3+} ; E, Cu^{2+} ; F, Fe^{3+} . [Right hand scale refers to Cu^{2+} and Fe^{3+} .]

transition metals, three lanthanides and one actinide studied, the lowest energy-allowed bands result from charge-transfer from the single group X to the metal. The unit slope of the plots in Fig. 1 also ensures that there is a reciprocal correlation between the bands

of pairs of anions with a series of metals. The points scatter surprisingly little about the line of unit slope, the major exceptions being those for $X = \text{H}_2\text{O}$. These occur at such a high energy that they are difficult to measure accurately.

DISCUSSION

Plots of the same type as Fig. 1 can be used in discussing a number of chemical problems. In the following sections they are applied to the study of stereochemistry, redox potentials, solvent effects, and band assignments.

Copper(II) Spectra.—The deviation of the two cupric monohalide points cannot be ascribed to experimental error because the spectra contained very well defined bands and the species are definitely characterized. A line joining the two points is approximately parallel to the line through the other cupric points but about 7 kK higher. One explanation for the difference between the halogens and the other complexes might be that they occupy a different type of site. Now it is well known that the cupric ion has a distorted environment in many solid compounds owing to the Jahn–Teller effect. Most frequently there are four ligands close to the metal and two further away, forming an elongated octahedron. Thus formally it is possible for a ligand to occupy one of two distinguishable sites. Where the co-ordination sphere contains two dissimilar ligands it has been suggested⁵ that the group producing the higher ligand field occupies the sites closer to the metal. Thus in both forms of $\text{Cu}(\text{NH}_3)_2\text{Br}_2$ where two ammonia molecules and four bromide ions are attached to the copper,⁶ the ammonia ligands are along a short axis. One form has two bromide atoms completing the equatorial plane and the remaining bromides axial, whereas in the other the four bromide atoms complete a flattened octahedron. No *X*-ray structure has revealed a group producing a higher ligand field lying at substantially greater distance than one of lower field. The halogens have a markedly weaker ligand field strength than oxygen donors and thiocyanate, and so in solution the halogen donors are much more likely to remain on the long axis. A comparison of the spectra of $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}\text{Br}^-$ shows that the longer the internuclear distance the higher the energy of the charge transfer transition. The band observed in the hexa-aquocupric ion must represent electron transfer from the closest water, and since the other oxygen donors and thiocyanate give a good 1 : 1 slope through this point in Fig. 1 we can assume that the lowest energy band represents charge transfer from the ligand *X* when the Cu–*X* distance is at its shortest. This explains the unusually high energies of the copper halide bands.

Correlation with Redox Potentials.—Dainton⁷ studied the charge-transfer spectra and redox potentials of a series of first-row transition metals. He found a good linear correlation between the edge of the intense absorption of the divalent metal perchlorates in aqueous solution and the $\text{M}^{3+}/\text{M}^{2+}$ standard potentials. These spectra result from charge transfer from M^{2+} to the solvent. The use of the edge rather than the band maximum is probably justified since the band half widths are not likely to change greatly from one element to another. In Fig. 2 we plot data for some of the species already discussed against the one electron reduction potentials for the metal ions.⁸ The plots, which are approximately linear, have slopes near to that observed by Dainton, but of course with the opposite sign. We find that 1 volt (redox) corresponds to 8 ± 1 kK, that is roughly to 1 eV.

One use of this correlation is to predict inaccessible reduction potentials where charge-transfer energies are known. For example, we know the position of the bands in TmCNS^{2+} and TmBr^{2+} in ethanol and by inserting these values in plots for other thiocyanates and bromides in ethanol (Fig. 2) we obtain two estimates of $E_0(\text{Tm}^{3+}/\text{Tm}^{2+})$, both in the region of 2.5 v. No experimental value for this potential has ever been reported but it is known to be well above that of Sm^{3+} , 1.55 v.

⁵ Wells, "Structural Inorganic Chemistry," Oxford University Press, Oxford, 3rd edn., p. 89.

⁶ Hanic, *Acta Cryst.*, 1959, **12**, 739; Hanic and Cakajdova, *ibid.*, **11**, 610.

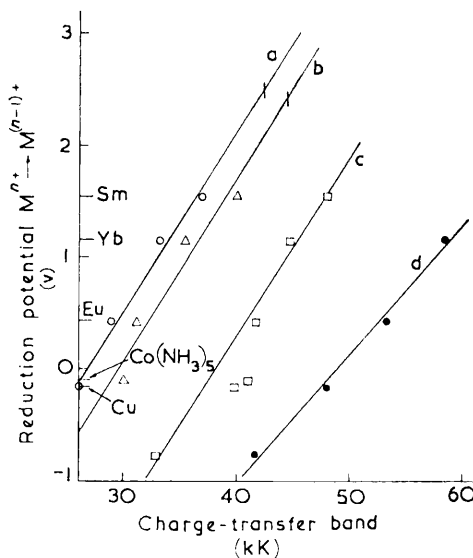
⁷ Dainton, *J.*, 1952, 1533.

⁸ Latimer, "Oxidation Potentials," Prentice-Hall, N.J., 2nd edn., 1952.

Ultraviolet Spectra of Thiocyanate Complexes.—We have already noted that when the charge-transfer energies of a series of metals with a given anion are plotted against the energies for the same metals with a second anion, straight lines of nearly unit slope are obtained. With other anions, similar plots may be used to test assignments by investigating the correlation with sets of bands known to originate from charge transfer.

Aqueous potassium thiocyanate has its first absorption maximum well above 50 kK (55 kK in the solid), but a number of thiocyanate complexes have an intense band in the near-ultraviolet region whose position is nearly independent of the oxidizing character of the metal ion. This band has been ascribed to a strongly perturbed ligand transition.⁹ In contrast, the intense visible absorption of $\text{Fe}(\text{NCS})(\text{H}_2\text{O})_5^{2+}$ is usually described as a

FIG. 2. Reduction potentials and charge-transfer bands. a, Thiocyanate (ethanol); b, Bromide (ethanol); c, Sulphate (aqueous); d, Water.



charge-transfer absorption. Elsewhere we have assigned the monosulphate frequencies in Fig. 1 to charge transfer,⁴ and Fig. 3 shows that there is a good 1 : 1 correlation with the corresponding thiocyanate frequencies. Furthermore, non-reducible ions such as La^{3+} , Gd^{3+} , and Zn^{2+} produce no such bands. There is little doubt, therefore, that the u.v. bands in the thiocyanates of all the reducible metals in Fig. 3 result from charge transfer to the metal.

Most of the data supporting the hypothesis of a perturbed ligand transition refer to Group VIII complexes where the ligand is bound to the metal through sulphur,¹⁰ and in contrast to the thiocyanates in Fig. 3 the metal-to-thiocyanate ratio is either four or six. In Fig. 4 we plot these band maxima against the lowest energy charge transfer bands of the chloride and bromide complexes of the appropriate stoichiometry. It can be seen that some small dependence on the metal remains.

The energy levels of linear triatomic molecules, including SCN^- , have been classified by Mulliken¹¹ and discussed at greater length by Walsh.¹² They agree that the highest occupied level, 2π in Mulliken's notation, has very little charge on the carbon atom (none in an A-B-A molecule) and consists mainly (entirely in A-B-A) of two pairs of out-of-phase $p\pi$ orbitals on the end atoms. In the lowest vacant molecular orbital charge is more evenly

⁹ Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon, Oxford, 1962, p. 196.

¹⁰ E.g., Mitchell and Williams, *J.*, 1960, 1912.

¹¹ Mulliken, *J. Chem. Phys.*, 1935, **3**, 720; *Rev. Mod. Phys.*, 1942, **14**, 204.

¹² Walsh, *J.*, 1953, 2260.

distributed between the three $p\pi(x)$ and $p\pi(y)$ orbitals, adjacent pairs of atomic orbitals being out of phase. In 2π , most of the charge will be placed on the nitrogen because of its greater electronegativity, so the lowest-energy absorption results in a net transfer of charge from nitrogen to carbon. Let us examine the effect on this absorption of attaching a reducible metal to either end of the ligand.

At the nitrogen end, an electron-attracting metal is expected to hinder the transfer of charge from nitrogen to carbon, raising the energy of the ligand transition. A metal atom at the sulphur end, however, will have the opposite effect, and stabilize the ligand excited state by withdrawing charge from the nitrogen. Thus we have an explanation for the metal dependence shown in Fig. 4. The small shifts compared with the halide ligand-to-metal charge-transfer spectra are accounted for if the thiocyanate transitions are localized

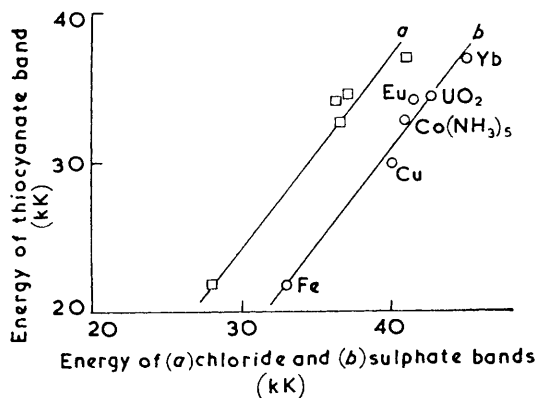
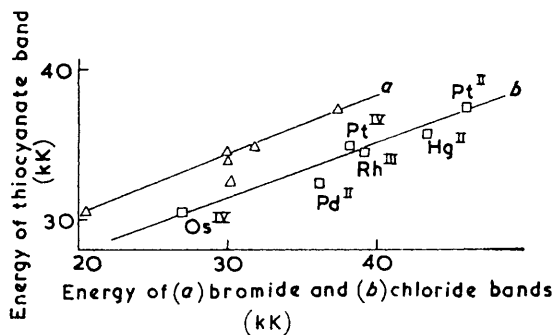


FIG. 3. Ultraviolet spectra of thiocyanate, chloride, and sulphate complexes.

FIG. 4. Ultraviolet spectra of chloride, bromide, and thiocyanate complexes.



on the ligand. Oxidizable metals bound to the nitrogen end of thiocyanate would be expected to have the same effect on the ligand transition as reducible metals bound to sulphur. The only reported spectra of such species, $\text{Co}(\text{NCS})_4^{2-}$ and $\text{Mo}(\text{NCS})_6^{3-}$, have their first intense bands at 32.8 and 31.0 kK, respectively.^{9,13} We cannot compare these with CoCl_4^{2-} and MoCl_6^{3-} spectra because the latter result from charge transfer to the metal. Referring to $\text{Co}(\text{NCS})(\text{H}_2\text{O})_5^+$, the band at 36.7 kK is not a ligand-to-metal charge-transfer because Fig. 3 would then predict a cobalt monosulphate band at about 44 kK, whereas solutions containing this species have no absorption below that of sulphate itself. The band in $\text{Co}(\text{NCS})(\text{H}_2\text{O})_5^+$, and probably also the one in $\text{Co}(\text{NCS})_4^{2-}$, is therefore the same perturbed ligand transition as in the Group VIII complexes. We have no clear data on the one remaining class of thiocyanate complex, that of an oxidizable metal bound through sulphur. One might expect that platinum(II) would act as a donor to thiocyanate rather

¹³ Lewis, Nyholm, and Smith, *J.*, 1961, 4597.

than an acceptor, but Gray and Ballhausen¹⁴ have assigned the tetrahalide bands as ligand-to-metal charge transfer and these, when plotted with the thiocyanate values (Fig. 4), give points on the line.

Our conclusion then is that the lowest-energy-allowed transitions of reducible metal thiocyanates bound through nitrogen should be of charge-transfer type, whilst reducible metal thiocyanates bound through sulphur, and oxidizable metal thiocyanates bound through nitrogen exhibit only the perturbed ligand band.

Spectra in Ethanol.—The difficulty in discussing spectra of complexes in non-aqueous solvents is that few studies have related them to stoichiometries and formation constants. We know that the charge-transfer spectra are a very sensitive function of the metal-to-ligand ratio. For example, CuBr^+ in aqueous solution has a single band at 36.0 kK, but as more bromide is added it splits into two, and further bands appear in the visible region as species up to CuBr_4^{2-} are formed. The energy of the first band observed as bromide is added to cupric perchlorate solutions decreases when ethanol replaces water in the solvent.¹⁵ We have to decide whether this is due to the formation of higher species or simply to the replacement of water by ethanol round the central atom. Both in water^{15a} and 90% ethanol,^{15c} the band has been proved to represent only CuBr^+ though the formation constant rises from 2 to 10 in the medium of lower dielectric constant. When excess of bromide is added the band shape changes in the same way in 100% ethanol as in water or 90% ethanol so the first species in ethanol is also CuBr^+ . We can therefore say quite definitely that the shift shown for CuBr^+ in Table 1 does represent the effect of solvation changes and not the formation of higher species.

This movement of ion-pair charge-transfer bands to lower energy as we change from water to ethanol is quite general. In Table 1 we present the band positions for copper(II) and uranyl halides and pseudohalides in the two solvents. The shifts are all very similar. Table 2 shows that for EuNCS^{2+} the change is not linear with percentage composition of solvent, most of the movement occurring between 90 and 100% ethanol. The much smaller shifts in ligand-field spectra show the same solvent dependence. To study the shifts with solvent we have used plots of the same type as Fig. 1. When the charge-transfer band positions of one ligand are plotted against those of another in the same solvent they form a straight line of almost unit slope, *e.g.*, in water, thiocyanate against sulphate, and in ethanol, thiocyanate against bromide. However, when we plot the ethanolic data for thiocyanate, chloride, and bromide against that for aqueous sulphate we get a set of parallel straight lines but their slope is no longer close to unity (data in Table 3, ref. 4).

We can seek an explanation for these observations in Jørgensen's concept of optical electronegativity.^{2,3} He holds that the energy of the charge-transfer band represents the difference in energy between ligand donor and metal acceptor orbitals. As we have already mentioned, the latter must be corrected for the energy required to change the spin multiplicity of the metal, and for the energy difference between the unsplit *d*-shell of the free ion and the orbital to which the electron is transferred in the complex. The latter is a function of the ligand field splitting parameter Δ . Thus the energy of the charge-transfer band is given by

$$\delta = E_L - E_M - (\text{spin-pairing correction}) + \Delta$$

The ligand and metal energies E_L , E_M are atomic parameters and independent of solvent. For the copper compounds the spin-pairing correction is zero, so on Jørgensen's theory the shift would be entirely attributable to a change in Δ . The shifts shown in Table 1 are over 3 kK for copper but the ligand-field band shift is only 0.14 kK so this cannot be the complete explanation. The spin-pairing correction for UO_2^{2+} is also zero ($5f^0 \rightarrow 5f^1$),

¹⁴ Gray and Ballhausen, *J. Amer. Chem. Soc.*, 1963, **85**, 260.

¹⁵ (a) Farrington, *J. Amer. Chem. Soc.*, 1952, **74**, 966; (b) Matsuo, *J. Chem. Soc. Japan*, 1961, **82**, 1330; (c) Barnes and Hume, *J. Phys. Chem.*, 1963, **67**, 526.

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TABLE 1.

Charge-transfer bands of 1 : 1 complexes (kK).

	Cu ²⁺			UO ₂ ²⁺		
	Water	Ethanol	Diff.	Water	Ethanol	Diff.
Cl	40·4	36·0	4·4	37·0	33·9	3·1
Br	36·0	32·3	3·7	33·3	30·0	3·3
NCS	29·4	26·0	3·4	34·5	29·4	5·1
CN				32·3	29·0	3·3

TABLE 2.

Solvent dependence of the europium monothiocyanate charge-transfer band.

% Ethanol	0	20	40	60	80	90	95	100
max. (kK)	34·5	34·5	34·5	33·9	33·3	32·8	32·5	29·4

but in the same way, we do not expect Δ to change by 3 kK between water and ethanol. A more probable explanation for the shifts is that solvents of lower dielectric constant will stabilize the less dipolar excited state, so that in going from water to ethanol the band moves to lower energy. The absorption bands of organic charge transfer complexes have a comparable solvent dependence, though since the excited state is usually more dipolar than the ground state, the bands move to lower energy¹⁶ in solvents of higher dielectric constant. The potential-energy difference between a 2·5 Å dipole in water (ϵ 80) and ethanol (ϵ 30) is roughly equivalent to 1 kK, so that coulomb stabilization of the ground state by the solvent provides a major contribution to the observed shift.

Besides the additive correction of Table 2, the fact that the plots do not have unit slope suggests that a multiplicative correction is also necessary. That such a correction applies only to the cation can be seen at once from the constancy of the shifts for different ligands with the same metal in Table 1, but Jørgensen's optical electronegativity theory only provides for additive corrections to the energy levels of the metal. Deviations from unit slope are well known in organic donor-acceptor complexes, when the band maxima for a given donor with a set of acceptors are plotted against the maxima in the complexes of another donor having, for example, the additional possibility of forming hydrogen bonds.¹⁷ Perhaps a similar explanation could be given for our own observations, but Mulliken¹⁸ has pointed out that the linear relationships frequently found between bands in organic donor-acceptor complexes are not obvious from theoretical arguments.

We thank Drs. C. K. Jørgensen and R. J. P. Williams for discussions, N.A.T.O. for a Fellowship (to J. C. B.), and the D.S.I.R. for a Studentship (to P. D.).

INORGANIC CHEMISTRY LABORATORY,
SOUTH PARKS ROAD, OXFORD.

[Received, October 1st, 1963.]

¹⁶ Foster and Hammick, *J.*, 1954, 2685.

¹⁷ Foster, *Trans. Faraday Soc.*, 1963, 59, 1059.

¹⁸ Reid and Mulliken, *J. Amer. Chem. Soc.*, 1954, 76, 3869.