Coordination Chemistry Reviews, 97 (1990) 261–270
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

PHOTOSELECTION STUDIES OF MONO-DIIMINE COMPLEXES: d-π^* and π–π^* EMITTERS

M.K. De Armond, M.L. Myrick, R. Pittman, and R.E. Des Enfants, II
Chemistry Department, New Mexico State University, Las Cruces, New Mexico 88003

SUMMARY

The photoselection spectra of a series of Ru(II) diimine complexes have been investigated. Mono-diimine complexes emitting from a d-π^* triplet show P values close to the linear-absorber linear-emitter limit (0.5), while complexes identified as π–π^* emitters show mixing of their d-π^* and π–π^* singlets as P values fail to reach the "pure" π–π^* emitter limit of -0.33. Comparative data as well as the interchromophoric coupling (ICC) model (ref. 3) are used to rationalize the results.

INTRODUCTION

In a series of papers, (refs. 1-9) the photoselection technique has been used to clarify and describe the localization of the emitting state energy in one Ru-diimine chelate ring for various diimine complexes (tris, bis, and mono). This experimental method in combination with a model (ref. 3) developed to quantitatively rationalize the magnitude of P_{max} (the maximum polarization value) obtained for the steady state excitation polarization spectra (SSExP) has succeeded in providing a framework to comprehend the anomalous P_{max} values measured for tris and bis diimine complexes for Ru(II) as well as the 0.1 P values measured at higher energies in the singlet metal to ligand charge transfer region (MLCT). Key to the interpretation of these data has been the P data for a few mono-diimine complexes, e.g., $[Ru(bpy)(py)_4]^{2+}$, where the observation of P_{max} values, in the MLCT singlet region, approaching the 0.5 limit expected for a linear-absorber linear-emitter system verifies that the charge transfer transition for this Ru-bpy chromophore is polarized along the Z-axis (Fig. 1) and that the emitting triplet obtains intensity only from this spin allowed transition. In the bis and tris complexes, the intermediate magnitude of P_{max} (between that expected for a linear-linear emitter and the 0.14 value for a planar-absorber planar-emitter system) indicates that non-Z-polarized triplet spin states acquire intensity, consequently reducing the magnitude of P_{max} to 0.23. The exact magnitude of this reduction results from coupling of the fundamental mono-bpy chromophore with the additional chromophores in the bis and tris complexes. These phenomena are modeled with the interchromophoric coupling (ICC) model (ref. 3).

0010-8545/90/$03.50

The P = 0.1 values on the high energy side of the singlet MLCT band for tris complexes are consistent with the existence of a delocalized orbital region (D_3 symmetry) for this singlet excited state along with the lower energy localized portion of this singlet excited state.

The prior work emphasizing bpy complexes has not commented in detail upon some anomalies which occur. For example, the $[Ru(i\text{-}biq)_3]^{2+}$ (i-biq = 2,2′-isobiquinoline) complex was first reported by Balzani and coworkers (ref. 4) as emitting from a triplet π–π^* state while the $[Ru(biq)_3]^{2+}$ (biq = 2,2′- biquinoline) complex (which is a d-π^* emitter) produces an anomalously high value (ref. 7) for P_{max} (0.38) at the red edge of the d-π^* absorption.

To clarify these anomalies and provide detail of the excited state symmetry, photoselection data has been collected and analyzed for a series of "pure" and "pseudo" mono-diimine complexes. Some of the P data is reported for the first time while data for others has been presented earlier.

If we define a monomeric species as a chromophoric unit possessing a single metal atom (Ru) and a diimine ligand with a low lying level capable of accepting charge from the metal, then complexes as diverse as $[Ru(bpy)(py)_4]^{2+}$ and $[Ru(bpz)(bpy)_2]^{2+}$ (Fig. 2) can be discussed .

The monomeric unit in the former complex is Ru(bpy) and in the latter it is Ru(bpz). For this work, we present data for $[Ru\,L(CN)_4]^{2-}$.

EXPERIMENTAL

Materials

$RuCl_3{\cdot}3H_2O$, 2,2′-bipyridine (Aldrich), $K_4Ru(CN)_6$ (Alfa), absolute ethanol (USI), THF (Aldrich), methanol (Fisher), acetone (Burdick + Jackson), dimethyl sulfate (Kodak), and pyridine were commercial products used without further purification. 2,2′-isobiquinoline (ibq), and $[Ru(ibq)_3][PF_6]_2$ were a generous gift from Dr. P. Belser. $Ru(bpy)_2Cl_2$ was available from previous studies. $K_2[Ru(bpy)(CN)_4]$ and $[Ru(bpy)(CH_3NC)_4][PF_6]_2$ were synthesized by the method of Scandola (ref. 10, 11). $K_2[Ru(ibq)(CN)_4]$ was prepared by Scandola's method (ref.10) except that 1:1 H_2O/THF was used as the solvent instead of 1:3 methanol/H_2O. $[Ru(bpy)(py)_4][ClO_4]_2$ (py=pyridine) was synthesized by the method of Krause (refs. 12, 13).

Spectroscopy

All emission and photoselection spectra were run at 77K in alcoholic or alcohol/H_2O glasses with an instrument described previously (ref. 14) but now automated with a Zenith Z-158 PC. Absorption spectra were obtained on a Cary 14 absorption spectrometer adapted for an Oxford Instruments DN-1704 $N_2(l)$ cryostat.

RESULTS

The photoselection, emission, and absorption spectra for light sensitive $[Ru(bpy)(py)_4]^{2+}$ are shown in Fig. 3. In Fig. 4 the emission, absorption, and photoselection spectra for $[Ru(bpy)_3]^{2+}$ are given and Fig. 5 shows the related data for $[Ru(bpy)(CN)_4]^{2-}$. Fig. 6 illustrates the unusual P spectra for the π–π^* emitter $[Ru(ibq)_3]^{2+}$. Fig. 7 shows the spectral data for $[Ru(ibq)(CN)_4]^{2-}$. Fig. 8 illustrates the spectral data for $[Ru(bpy)(CH_3NC)_4]^{2+}$, a π-π^* emitter.

DISCUSSION

Monomeric complexes:$d\pi^*$ emitters.

For the purpose of this discussion, it is necessary to define a monomeric species as a chromophoric unit possessing a single metal atom (Ru) and a single diimine ligand with a low-lying π^*-orbital, and containing no other ligands with low-lying levels capable of accepting charge from the metal. This allows electron density to be completely localized in the MLCT states on the single chelate ring of interest.

The difficulty of producing a stable monomeric complex has made studies of the individual chromophore rare (ref. 1). The light sensitive complex $[Ru(bpy)(py)_4]^{2+}$ was described first by Krause (ref. 12), who was not certain of the intermediate steps in the synthesis (ref. 13). The data for this complex in (Fig. 3) is different from that reported by Carlin (ref. 1) principally due to difficulties with impurities. The synthesis of this complex, unfortunately, appears to result in production of $[Ru(bpy)_2(py)_2]^{2+}$, an impurity with virtually the same physical characteristics as the desired product, but with different polarization properties. It was not possible to obtain this complex in ideal purity, but its purity was sufficient for this analysis.

The ^{1}MLCT transition of the Ru-py chromophore appears in the UV region of the spectrum, thus allowing the entire visible region to be dominated by the absorbance of the Ru-bpy chromophore, despite the fact that the intensity of this transition is only a fraction that of the Ru-py absorbance. A notable feature of the absorption spectroscopy of $[Ru(bpy)(py)_4]^{2+}$ is that the visible ^{1}MLCT transition possesses the same absorption profile as that of the $[Ru(bpy)_3]^{2+}$ ion. This indicates that the interaction energy between chromophoric units in the tris-chelated species is small relative to the resolution of the technique.

By contrast, the absorbance of the Ru-py unit is very different from that of the Ru-bpy unit, thus indicating that interactions between the two pyridine units of bipyridine are very large. This large interaction between the pyridyl rings demonstrates the distinct nature of the bipyridine chromophore from that of pyridine. In practical terms this means that the promoted electron is delocalized between the pyridyl subunits rather than localized on a distinct subunit. The SSExP spectroscopy of this complex helps to explain some properties of the chromophore. The relatively plain profile leads directly to

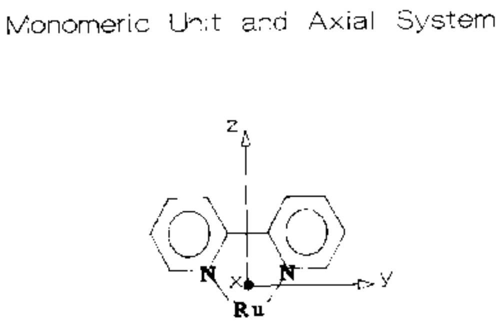


Fig. 1. Mono unit and Axis System A diagram of the Ru-bpy monomer unit with the Z-axis defined as the metal-ligand axis, while Y is parallel to the long axis of the complex.

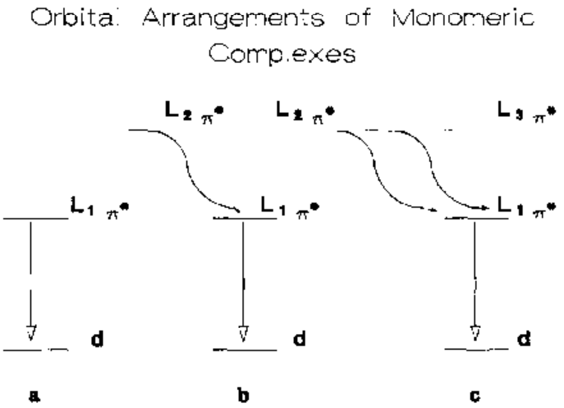


Fig. 2. Orbital Arrangements of Monomeric Complexes Three possible arrangements which produce monomeric or pseudo-monomeric complexes. (a). A true monomeric complex with only a single diimine chelate ligand. (b). A second diimine chelate with a π^* orbital at much higher energy produces a pseudo-monomeric complex luminescing from the lowest-lying chromophore. In (c), this is extended with two additional diimine chromophores whose π^* orbitals are significantly higher in energy.

Figure 3.

$[Ru(bpy)(py)_4](ClO_4)_2$ EtOH

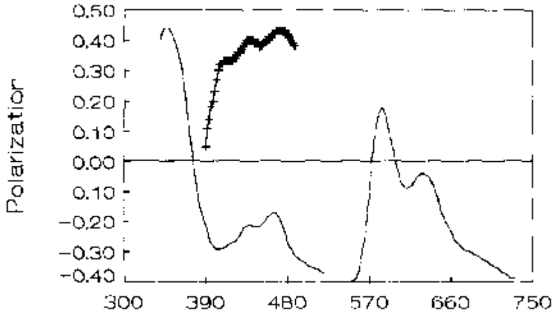


Figure 4.

$[Ru(bpy)_3]^{2+}$ in EtOH at 77K

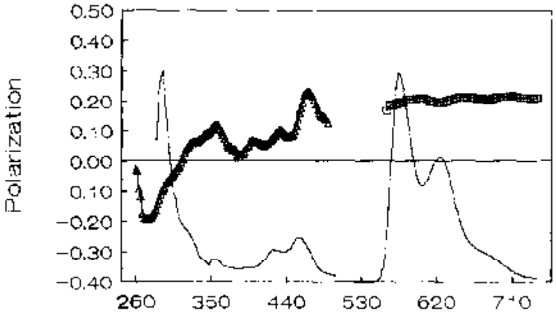


Figure 5.

$K_2[Ru(bpy)(CN)_4]$ EtOH 77K

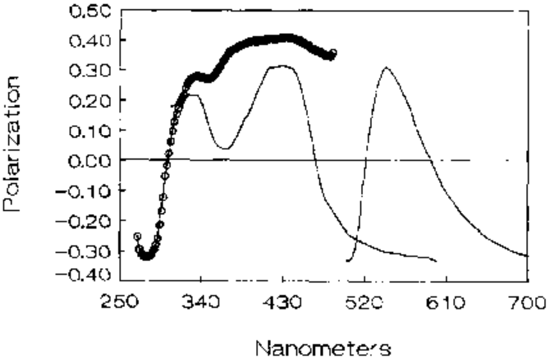


Figure 6.

$[Ru(ibiq)_3](PF6)_2$ in EtOH

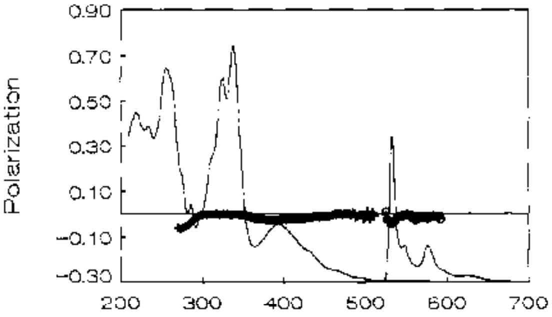


Figure 7.

$K_2[Ru(ibiq)(CN)_4]$ EtOH 77K

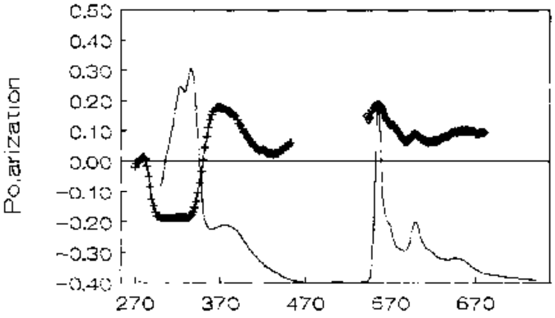
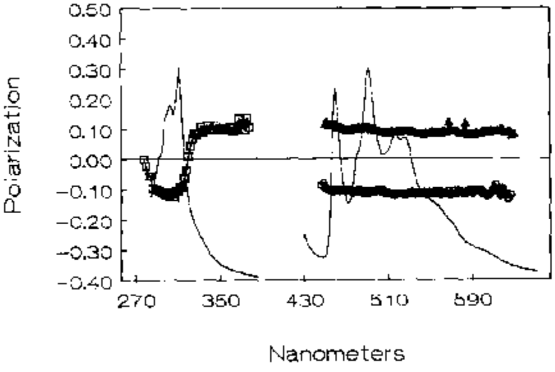


Figure 8.

$[Ru(bpy)(CNMe)_4]^{2+}$ at 77K



simple approximations of the polarization and symmetry characteristics of the Ru-bpy unit.

As shown, the photoselection profile of $[Ru(bpy)(py)_4][ClO_4]_2$ rises from a low value near the Ru-py absorbance to a very positive value across the Ru-bpy ^{1}MLCT. The maximum value of P for this complex was 0.43, close to the positive limit of +1/2, seen only for parallel linear-absorption and emission oscillators. This demonstrates that the absorption and emission oscillators at this point in the absorption profile are approximately linear and parallel to one another. Since the emission oscillator is independent of excitation wavelength (shown by the excitation wavelength independence of emission energy), the large value of polarization across the entire ^{1}MLCT to bipyridine indicates a single major polarization component in the absorption of this state. This component is assumed to be polarized along the Z-axis. The small amount of structure seen in the SSExP is principally due to the residual impurity existing in the complex, as well as some contribution from the very intense and negatively polarized ^{1}MLCT-pyridine transition which tails into the visible region. Thus we conclude that polarization of the ^{1}MLCT-bipyridine transition is linear throughout for this complex.

The data shown (Fig. 5) for $K_2[Ru(bpy)(CN)_4]$ corroborates the preceding conclusions. We find for this complex that the ^{1}MLCT transition does not possess the typical absorption profile seen for the Ru-bpy unit in other complexes. However, this complex demonstrates a large degree of sensitivity to the solvent environment even in glassy media (ref. 10). Thus the bandshape is likely influenced by true solvent heterogeneity and/or involvement of the solvent in the excited state. This solvatochromicity is due to the variable sigma-donor and pi-acceptor properties of the CN^- ligand depending upon coordination of the unbound nitrogen with solvent molecules. Also conceivable is participation in the MLCT transition by the CN^- ligands, as they perturb the metal orbitals via their strong pi-acceptor ability. Thus the transfer of charge from the metal would not involve orbitals purely localized on the metal, but also a small component deriving from the CN^- π^* orbitals. At present, a simple procedure for determining the contribution of the latter process is not known. Regardless of the modification of the absorption profile, the SSExP of this complex remains simple. Across the $\pi-\pi^*$ transition of the ligand, polarization achieves a negative value, $P = -0.32$. This value is likely to be as close to the negative polarization limit of -1/3 as may be practically determined, since depolarizing effects of lattice vibrations and the non-ideality of the polarizers used for the experiment are limiting. Previous studies have shown that this transition of the ligand is polarized along the long (Y) axis of the molecule (refs. 15-16). Using this as a basis one may conclude that the emission oscillator cannot include any appreciable intensity along this axis. This is done by recognizing that any parallel component in the absorption and emission oscillators will give rise to a positive component of P, which will increase the photoselection values from the negative limit. A value of P = -1/3 indicates purely orthogonal absorption and emission polarizations. A similar statement holds for $[Ru(bpy)(py)_4]^{2+}$, however, due to the overlap of the ^{1}MLCT-pyridine transition with that of the π–π* band seen here, definitive data cannot be obtained for this complex.

The SSExP values rise rapidly from the negative limit over the π–π* absorbance, and form a positive and unstructured region across the entire ^{1}MLCT transition. The fact that this photoselection region is unstructured and positive confirms that emission and charge-transfer absorption are dominantly linear processes. Indeed, the long wavelength range for which P is very large indicates that overlapping and perpendicular absorption polarizations do not contribute to the values obtained. This leads to the conclusion that the absorption oscillator is nearly exactly linear; the fact that the d–π* P does not quite reach +1/2 and the π–π* polarization was indistinguishable from -1/3 indicates that the emission oscillator possesses a mixture of polarizations. This is confirmed by the slight reduction in polarization as excitation occurs into the triplet absorbance region, resulting from mixed oscillators in absorbance and emission. Since it was previously shown that no emission intensity could be occurring which is polarized along the long (Y) axis of the ligand, we must conclude that the emission oscillator possesses polarization which is dominantly Z-axis directed, but also contains a component along the out-of-plane direction of the ligand. This indicates Z, X emission for the complex.

For this C_{2v} unit, the metal t_{2g} orbital set is split into three distinct orbitals, giving rise to three possible emitting orbital triplet states (assuming involvement of only one π* orbital on the single ligand of the complex). These orbitals are members of the a_1, a_2 or b_1 representations in C_{2v}. Since the lowest π* orbital of the ligand is the φ orbital of b_1 symmetry (ref. 17), this gives rise to orbital states of B_1, B_2, and A_1 symmetry, respectively.

The triplet spin functions belong to C_{2v} symmetry in the a_2, b_1, and b_2 representations. Thus for the orbital states derived above, only one, the B_2 state, has the possibility of oscillator strength in two orthogonal directions neither of which is the long Y-axis direction of the ligand, without the simultaneous intervention of a non-totally symmetric vibration. On this basis, we assign the lowest emitting state of this complex and, by analogy, that of most of the other complexes as the B_2 state, with parentage in the lowest π* orbital of bipyridine and the dπ orbital of a_2 symmetry.

The question of whether the two major absorption bands in the ^{1}MLCT transition represent distinct electronic transitions is still open, though evidence now strongly suggests vibronic origins for the higher energy band. The suggestion by Ferguson et al. (refs. 18, 19), that the high energy band derives from the χ orbital of bipyridine has previously been shown incorrect; indeed this transition does occur, but at much higher energy (ref. 20). The conclusion of Ceulemans and Vanquickenborne (ref. 21), that the two transitions derive from metal electron promotion to exciton levels of the three bipyridines, is inconsistent with the observation of the same transitions in monomeric complexes. The final possibility for distinct electronic transitions is that these bands derive from promotion of electrons in distinct metal orbitals, split by low symmetry. This, however, seems unlikely since the separation of the two bands remains relatively constant, and appears independent of the relative strength of the ligand field.

Other "monomeric" complexes such as $[Ru(bpy)_2(bpz)]^{2+}$ (bpz=2,2′-bipyrazine) and $[Ru(bpy)_2(pq)]^{2+}$ (pq=2,2′-pyridylquinoline) have been reported in the literature (ref. 3). These species confirm some of the conclusions above. Such complexes are monomeric in nature despite containing three chromophores since only a single chromophore is involved in the luminescence. In addition, the absorption profiles for these complexes are well separated and distinct. These facts derive from the low energy of the π^* orbitals of bpz and pq relative to bpy, as shown by cyclic voltammetry of the mixed ligand species (ref. 22). These complexes possess large positive polarizations for excitation into the ^{1}MLCT of the emitting chromophore also indicative of linear oscillators in absorption and emission.

The π–π^* emitters

The tris $[Ru(i\text{-}biq)_3]^{2+}$ complex has been determined to be a π-π^* emitter and the emission spectra for this complex are clearly different from that of the $[Ru(bpy)_3]^{2+}$ species. Moreover, the photoselection spectra for the complex is slightly negative across the MLCT band (ref. 3). Such a result is broadly consistent with expectations that the π–π^* emission would be out of plane, thus perpendicular to the MLCT transition polarization which should still be in plane (if localized). The MLCT band is skewed to higher energy in the complex than for the d-π^* emitters and such a circumstance results in an interaction between the π–π^* and the high energy d-π^* state. This matter has been reported elsewhere (ref. 4).

The spectra for $[Ru(i\text{-}biq)(CN)_4]^{2-}$ help to clarify the situation for the tris π–π^* emitters. The emission structure and energy for the mono-complex is similar to that of the tris i-biq complex verifying the π–π^* emission identity of the mono-complex. The photoselection spectra across the relatively high energy d-π^* singlet absorption is now more positive than for the $[Ru(i\text{-}biq)_3]^{2+}$ complex and does not reach the -0.33 limit expected for two perfectly orthogonal transitions. Since the ligand π–π^* transition is at much higher energy, the origin of the deviation from expectation cannot be trivial overlap of transitions. More likely some mixing of the singlet π–π^* and d-π^* transition moments may be occurring to produce the resulting P values. The photoselection spectra for the $[Ru(bpy)(CH_3NC)_4]^{2+}$, also identified as a π–π^* emitter, can be readily understood by comparison with other π–π^* emitters since the SSExP contour is similar for both species. Some further verification of the mixed emission dipole rationale can be derived from the deviation from the limit of the SSExP for the π–π* absorption of this species. For both complexes, the P contour does not reach the -0.33 value expected for a pure π–π* triplet with a pure π–π* singlet. The photoselection results for the π–π* emitting [Ru(bpy)(CNH)$_4$]$^{2+}$ are similar but are not reported since reproduction of results was hampered by the shattering of sample tubes upon cooling to 77K.

CONCLUSIONS

The excitation polarization values (SSExP) for the mono-diimine complexes of Ru(II) emitting from a d-π* triplet produce P values approaching the linear-absorber linear-emitter limit.

Analysis of the emission symmetry for these complexes indicates that this emitting state has overall B$_2$ symmetry. In contrast, the SSExP spectra for the π–π* emitters suggest that the d-π* and π–π* singlets mix to produce P values that deviate from expectation for a pure π–π* emitter.

REFERENCES

1 Carlin, C. M.; De Armond, M. K. *Chem. Phys. Lett.* **1982**, *89*, 297.
2 De Armond, M.K.; Myrick, M. L.; R. L. Blakley *J. Am. Chem. Soc.* **1987**,*109*, 2841.
3 De Armond, M. K.; Arthur, M. L.; Blakley, R. L.; Myrick, M. L. *J. Am. Chem. Soc.* **1988**,*11*, 1325.
4 Barigelletl, F.; Belser, P.; von Zelewsky, A.; Juris, A.; Balzani, V. *J. Phys. Chem.* **1985**,*89*, 3680.
5 Myrick, M. L.; Blakley, R. L.; De Armond, M. K. *Inorg. Chem.* **1988**, *27* , 589.
6 Blakley, R. L.; Myrick, M. L.; De Armond, M. K. *Chem. Phys. Lett.* **1989**,*157*, 73.
7 Blakley, R. L.; Myrick, R. L.; De Armond, M. K. *J. Phys. Chem.* **1989**, *93*, 3936.
8 Myrick, M. L.; De Armond, M. K. *J. Phys. Chem.* In press (1989).
9 Myrick, M. L.; Blakley, R. L.; De Armond, M. K. *J. Am. Chem. Soc.* In press (1989).
10 Bignozzi, C.A.; Chiorboli, C.; Indelli, M.T.; Rampi Scandola, M.A.; Varani, G.; Scandola, F. *J. Am. Chem. Soc.* **1986**, *108*, 7282.
11 Indelli, M. T.; Bignozzi, C. A.; Marconi, A.; Scandola, F. *J. Am. Chem. Soc.* **1988**, *110*, 7381.
12 a) Krause, R. A. *Inorg. Chim. Acta.* **1977**, *22*, 209. b) Krause, R. A. *Struct. Bonding* **1987**,*67*, 1.
13 Krause, R. A. *Inorg. Chim. Acta.* **1978**, *31*, 241.
14 Carlin, C. M.; Hanck, K. W.; De Armond, M. K. *Rev. Sci. Instrum.* **1981**, *52*, 137.
15 Mason, S. *Inorg. Chim. Acta.* **1965**, *2*, 89.
16 Ohno, T.; Kato, S. *Bull. Chem. Soc. Japan*, **1974**, *47* (12), 2953.
17 Konig, E; Kremer, S. *Chem. Phys. Lett.* **1970**, *5*, 87.
18 Felix, F.; Ferguson, J.; Güdel, H.; Ludi, A. *Chem. Phys. Lett.* **1979**, *62* (No. 5), 153.
19 Felix, F.; Ferguson, J.; Güdel, H.; Ludi, A. *J. Am. Chem. Soc.* **1980**,*102*, 4096.
20 Honazaki, I.; Nagakura, S. *Inorg. Chem.* **1969**, *8*, 648.
21 Ceulemans, A.; Vanquickenborne, L. *J. Am. Chem. Soc.* **1983**,*103*, 2238.
22 Ohsawa, J.; Hanck, K.; De Armond, M. K. *J. Electroanalytical Chem.* **1984**,*175*, 929.