Coordination Chemistry Reviews, 129 (1994) 195–245

Chromium(III) cyano-am(m)ine complexes

Edoardo Zinato
Dipartimento di Chimica, Universitá di Perugia, 06100 Perugia (Italy)

(Received 29 January 1993)

CONTENTS

Correspondence to: E. Zinato, Departimento di Chimica, Universitá di Perugia, 06100 Perugia, Italy.

ABSTRACT

The review deals with various aspects of a relatively young family of mixed-ligand complexes comprising mono- and polynuclear species, the latter cyano- or isocyano-bridged. Compared with other chromium(III) acido-am(m)ines, these exhibit atypical ground-state and excited-state properties arising from coordination of the CN^- groups. A systematization is presented of the preparative procedures, followed by a collection of the most relevant structural results. The electronic absorption and emission spectra are then discussed, and the solution reactivity (cyanide aquation and isomerization) is reviewed. Particular attention is devoted to the photochemistry and photophysics of these compounds. The uncommon ligand-field state sequences give access to photolabilization patterns and photostereochemistries that are complementary to the usual occurrence, providing significant test cases for the photolysis models. In addition, the long-lived solution phosphorescence makes possible accurate studies of the possible doublet-state decay routes, as well as of energy transfer in supramolecular systems. The available data are summarized in 11 tables, and reference to the literature is made by 117 citations.

ABBREVIATIONS

bcs	3-bromo-*d*-camphor-8-sulphonate ion
bpy	2,2′-bipyridine
chxn	1,2-diaminocyclohexane
cyclam	1,4,8,11-tetraazacyclotetradecane
dmf	*N*,*N*-dimethylformamide
dmso	dimethyl sulphoxide
edta	ethylenediaminetetraacetate ion (Y^{4-})
en	1,2-diaminoethane
phen	1,10-phenanthroline
pn	1,2-diaminopropane
sep	1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane
tacn	1,4,7-triazacyclononane
tet*a*	5,12-*meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane
tet*b*	5,12-*rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane
3,2,3-tet	1,10-diamino-4,7-diazadecane
tmpa	tris(2-pyridylmethyl)amine
tms	tetramethylenesulphone (sulpholane)
tn	1,3-diaminopropane
[15]aneN_4	1,4,8,12-tetraazacyclopentadecane

1. INTRODUCTION

The significance of ammine and amine complexes in Cr(III) coordination chemistry is evident in the comprehensive 1970 review by Garner and House [1]. Other surveys have covered particular aspects of these compounds, such as electronic spectra [2–4], magnetochemistry [5], ligand substitution mechanisms [6–9], photochemistry [10–14] and photophysics [15], or specific families such as the fluorodiamine [16] and the hydroxo-bridged species [17].

Unlike their Co(III) analogues [18], the cyanoam(m)ine complexes of Cr(III) were unknown until 1975. Especially during the past decade, a variety of such compounds has been synthesized and studied from several points of view. They may well be regarded as a peculiar class of acidoam(m)ines, since a unique combination of properties makes CN^- stand out among the common ligands, affecting both the ground-state and the excited-state behaviours: (1) the great stability of the metal—ligand bond, (2) the π-acceptor character, (3) the high basicity enabling extensive protonation of the coordinate group, (4) the considerable trans effect, (5) the bridging ability, (6) the top spectrochemical position and (7) the large nephelauxetic effect. Various monographs on transition-metal cyano complexes [18–20] have summarized the features of CN^- as terminal and bridging group.

This overview covers the investigations performed on mono- and polynuclear cyano complexes having NH_3 (ammines) or its derivatives (amines) as ligands. Borderline systems, such as diimine complexes and isocyano-bridged Cr(III)-am(m)ines, are also considered. The literature was searched to April 1992.

2. SYNTHESES

The majority of known Cr(III) cyanoam(m)ine complexes are mono- and dicyano cationic species. Most of the preparations involve CN^- coordination to Cr(III) already bound to the desired am(m)ines, which is frequently not as facile as that of other common monodentate acido groups. Therefore, original methods have often supplemented standard routes to acidoam(m)ines.

An example of a general procedure, impracticable with CN^-, is replacement of H_2O by anions in $CrN_5(H_2O)^{3+}$, $CrN_4(H_2O)_2^{3+}$ and $CrN_4(H_2O)X^{2+}$ species, (N = ammonia or amine nitrogens) in aqueous and non-aqueous media, and sometimes upon heating of solid salts where the counterion is the entering group [1]. Ready deprotonation of coordinated water by the basic CN^- reagent makes the Cr—OH bonds even stronger than the Cr—OH_2 bonds; moreover, am(m)ine loss from the unstable hydroxo complexes overcomes anation. Such a nuisance is not so crucial with Co(III) [18], whose preference for nitrogen donors, relative to oxygen donors, is larger than that of Cr(III).

Although the cyanoam(m)ines are not numerous compared with other Cr(III) families, a systematization of the preparative methods is attempted, as summarized in Table 1.

2.1 CN^- anation of Cr(III)-am(m)ines in aqueous solution

Despite the common use of water in anation reactions of metal-am(m)ine complexes, the relatively few successful preparations show the limited utility of this solvent in binding CN^- to Cr(III). Likely disadvantages are (1) competition of H_2O as a ligand of particularly high affinity for Cr(III), and (2) hydrolysis of CN^- that removes some of the reagent and, more importantly, alkalinizes the medium, inducing complex decomposition with formation of hydroxo- and oxo-containing species.

Mixtures of *cis*- and *trans*-$Cr(en)_2(CN)_2^+$ were first prepared from aqueous $Cr(en)_3^{3+}$ and NaCN in the presence of charcoal. The isomers were separated by ion-exchange chromatography and precipitated as the perchlorate or chloride salts [21]. This method was later found to be poorly reproducible, specially as to production of the trans compound [22].

One early attempt to synthesize *trans*-$Cr(NH_3)_4(CN)_2^+$ consisted of treating *trans*-$Cr(NH_3)_4(dmso)_2^{3+}$ with excess NaCN in water: the product accumulated owing to the low solubility of its cyanide salt. During anation of *cis*-$Cr(NH_3)_4(dmso)_2^{3+}$ under the same conditions, *cis*-$Cr(NH_3)_4(dmso)(CN)^{2+}$, but not the *cis*-dicyano complex, could be isolated [23]. The failure to obtain *trans*-$Cr(NH_3)_4(dmso)(CN)^{2+}$ in the former case and *cis*-$Cr(NH_3)_4(CN)_2^+$ in the latter was attributed to the trans-labilizing ability of cyanide. In the trans system, entry of the first CN^- is followed by quick replacement of *trans*-dmso by another CN^- or by H_2O. In the cis system, further anation of *trans*-NH_3 groups results in formation of very soluble anionic complexes [23]. These preparations are stereoretentive, in agreement with the aqueous behaviour of Cr(III) [7,24], but the product yields are generally lower than in other media.

The edta species $Na_3[Cr(Y)(H_2O)(CN)_2]\cdot 4H_2O$ was prepared by anation of $Cr(YH)(H_2O)$ in aqueous solution [25]. It was somewhat surprising that coordinated water was firmly held, although this occurrence seems common to Cr(III)-edta compounds.

The diimine ions *cis*-$Cr(bpy)_2(CN)_2^+$ and $Cr(phen)(CN)_4^-$ were synthesized in water using *cis*-$Cr(bpy)_2Cl_2^+$ and *cis*-$Cr(phen)_2Cl_2^+$ as starting materials [26]. The yields were again much smaller than those for coordination of acido groups other than CN^-. $Cr(phen)_2(CN)_2^+$ could only be obtained as the double complex salt $[Cr(phen)_2(CN)_2][Cr(phen)(CN)_4]$.

2.2 CN^- anation of Cr(III)-am(m)ines in aprotic solvents

This is the most widely employed procedure. In addition to avoiding the above-mentioned drawbacks of water, dipolar aprotic solvents usually enhance ion pairing

TABLE 1

Summary of preparative methods[a]

Complex	Method	Precursor[b]	Medium	Ref.
$Cr(NH_3)_5(CN)^{2+}$	2.2	$Cr(NH_3)_5(dmso)^{3+}$	dmso	27
trans-$Cr(NH_3)_4(CN)_2^+$	2.1	*trans*-$Cr(NH_3)_4(dmso)_2^{3+}$	H_2O	23
	2.2	*t*/*c*-$Cr(NH_3)_4(dmso)_2^{3+}$	dmso	23
		t/*c*-$Cr(NH_3)_4(dmso)Cl^{2+}$	dmso	23
	2.3	$Cr(NH_3)_5(CN)^{2+}$	CH_3OH	39
cis-$Cr(NH_3)_4(CN)_2^+$	2.2	*t*/*c*-$Cr(NH_3)_4(dmso)_2^{3+}$	dmso	23
		t/*c*-$Cr(NH_3)_4(dmso)Cl^{2+}$	dmso	23
trans-$Cr(en)_2(CN)_2^+$	2.1	$Cr(en)_3^{3+}$	H_2O	21
	2.2	*trans*-$Cr(en)_2(OSO_2CF_3)_2^+$	dmso	34
cis-$Cr(en)_2(CN)_2^+$	2.1	$Cr(en)_3^{3+}$	H_2O	21
	2.2	*trans*-$Cr(en)_2Br_2^+$	dmf	22
		trans-$Cr(en)_2(OSO_2CF_3)_2^+$	dmso	34
		$Cr(en)_3^{3+}$	dmso	35
	2.4	$CrCl_3 \cdot 6H_2O$	H_2O	40
		$CrCl_3 \cdot 6H_2O$	CH_3OH	22
cis-$Cr(pn)_2(CN)_2^+$	2.4	$Cr(H_2O)_6^{3+}$	pn	41
trans-$Cr(tn)_2(CN)_2^+$	2.2	*trans*-$Cr(tn)_2Br_2^+$	dmso	31
trans-$Cr(3,2,3\text{-tet})(CN)_2^+$	2.2	*trans*-$Cr(3,2,3\text{-tet})Cl_2^+$	dmso	30
trans-$Cr(cyclam)(CN)_2^+$	2.2	*t*/*c*-$Cr(cyclam)Cl_2^+$	dmso	28
trans-Cr(tet*a*)$(CN)_2^+$	2.2	*trans*-Cr(tet*a*)Cl_2^+	dmso	29
cis-Cr(tet*b*)$(CN)_2^+$	2.2	*cis*-Cr(tet*b*)$(H_2O)_2^+$	dmso	32
cis-$Cr(bpy)_2(CN)_2^+$	2.1	*cis*-$Cr(bpy)_2Cl_2^+$	H_2O	26
$Cr(tacn)(CN)_3$	2.2	$Cr(tacn)Br_3$	dmso	36
		$Cr(tacn)Cl_3$	dmso	32
		$Cr(tacn)(OSO_2CF_3)_3$	dmso	32
$Cr(pn)(CN)_4^-$	2.4	$Cr(H_2O)_6^{3+}$	pn	42
$Cr(phen)(CN)_4^-$	2.1	*cis*-$Cr(phen)_2Cl_2^+$	H_2O	26
$Cr(NH_3)(CN)_5^{2-}$	2.6	$Cr(CN)_6^{3-}$	CH_3OH	45
trans-$Cr(NH_3)_4(H_2O)(CN)^{2+}$	2.5	*trans*-$Cr(NH_3)_4(CN)_2^+$	H_2O	39
cis-$Cr(NH_3)_4(H_2O)(CN)^{2+}$	2.5	*cis*-$Cr(NH_3)_4(CN)_2^+$	H_2O	23
cis-$Cr(NH_3)_4(dmso)(CN)^{2+}$	2.1	*cis*-$Cr(NH_3)_4(dmso)_2^{3+}$	H_2O	23
	2.2	*t*/*c*-$Cr(NH_3)_4(dmso)_2^{3+}$	dmso	23
trans-$Cr(NH_3)_4Cl(CN)^+$	2.3	*trans*-$Cr(NH_3)_4(dmso)Cl^{2+}$	CH_3OH	38
trans-$Cr(NH_3)_4(NCS)(CN)^+$	2.3	*trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$	CH_3OH	38
trans-$Cr(NH_3)_4F(CN)^+$	2.3	*trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$	CH_3OH	38
cis-$Cr(en)_2(H_2O)(CN)^{2+}$	2.5	*cis*-$Cr(en)_2(CN)_2^+$	H_2O	40
mer-1,6-CN-$Cr(NH_3)_3(H_2O)(CN)_2^+$	2.5	*trans*-$Cr(NH_3)_4(CN)_2^+$	H_2O	43
mer-1,2-CN-$Cr(NH_3)_3(H_2O)(CN)_2^+$	2.5	*t*/*c*-$Cr(NH_3)_4(CN)_2^+$	H_2O	43
fac-$Cr(NH_3)_3(H_2O)(CN)_2^+$	2.5	*cis*-$Cr(NH_3)_4(CN)_2^+$	H_2O	44
$Cr(Y)(H_2O)(CN)_2^{3-}$	2.1	$Cr(YH)(H_2O)$	H_2O	25
$(tmpa)(CN)CrOCr(CN)(tmpa)^{2+}$	2.2	$(tmpa)Cr(OH)_2Cr(tmpa)$	CH_3CN	37

[a] Cyano-bridged polynuclear complexes (Sects. 2.7 and 2.8) not included.

[b] *t*/*c* denotes production of the same product, irrespective of the *trans* or *cis* configuration of the starting material.

between the reagents and hence favour anation. Dimethyl sulphoxide proves particularly suitable to this purpose. Even oxygen-bound ligands are efficiently replaced by CN^- when such ligands are themselves aprotic molecules.

The $Cr(NH_3)_5(CN)^{2+}$ prototype was, in fact, prepared by reacting $Cr(NH_3)_5(dmso)^{3+}$ with NaCN in dmso solution [27]. Similarly, *trans*- and *cis*-$Cr(NH_3)_4(CN)_2^+$ were obtained from either $Cr(NH_3)_4(dmso)_2^{3+}$ or $Cr(NH_3)_4(dmso)Cl^{2+}$ species [23].

Several dicyanoamines were synthesized by displacing relatively labile halogenide ligands. Thus, *trans*-$CrN_4(CN)_2^+$ complexes, where N_4 = cyclam [28], tet*a* [29] and 3,2,3-tet [30], were obtained in dmso from the corresponding *trans*-$CrN_4Cl_2^+$ ions; under analogous conditions, *cis*-$Cr(en)_2(CN)_2^+$ [22] and *trans*-$Cr(tn)_2(CN)_2^+$ [31] were prepared starting from *trans*-$CrN_4Br_2^+$ compounds.

Cis-Cr(tet*b*)$(CN)_2^+$ was formed by heating *cis*-Cr(tet*b*)$(H_2O)_2^{3+}$ near the boiling point of dmso and subsequent reaction with NaCN at a lower temperature [32]. Evidently, a bis-dmso intermediate was the species undergoing anation in this case also.

Mixtures of *trans*- and *cis*-$Cr(en)_2(CN)_2^+$ were obtained in high yields by exploiting the lability [33] of trifluoromethanesulphonate (triflate) in the *trans*-$Cr(en)_2(OSO_2CF_3)_2^+$ precursor [34].

Even a diamine can be sometimes displaced by CN^- in dmso, as in the conversion of $Cr(en)_3^{3+}$ to *cis*-$Cr(en)_2(CN)_2^+$ [35].

The stereochemical change to which Cr(III) is prone in dipolar aprotic media may be a complicating factor that contrasts with the usual stereorigidity in water [7,24]. Upon interaction of either $Cr(NH_3)_4(dmso)_2^{3+}$ isomer with CN^-, approximately equimolar amounts of *trans*- and *cis*-$Cr(NH_3)_4(CN)_2^+$ eventually form, irrespective of the initial configurations [23]. CN^- seems to play a special role here. While each of the parent isomers is fairly stable in dmso, addition of CN^- (but not of Cl^-, Br^- and NCS^-) to the trans compound induces fast and virtually complete rearrangement to cis before anation takes place: *cis*-$Cr(NH_3)_4(dmso)(CN)^{2+}$ is the sole first-step product. Entry of the second cyanide is then accompanied by partial cis→trans isomerization. The cis geometry of the 3+ and 2+ charged dmso complexes is thought to be stabilized by ion pairing with CN^-, whereas mutual CN^- repulsion would shift the isomeric equilibrium toward the trans form in the 1+ charged dicyano product [23].

Geometrical change is sometimes complete and irreversible: for example, reaction of *trans*-$Cr(en)_2Br_2^+$ with KCN in dmf was reported to lead exclusively to *cis*-$Cr(en)_2(CN)_2^+$ [22].

Bulky amine ligands appear to favour trans configurations. This is retained, at least on a preparative scale, during the syntheses of the cyclam [28], tet*a* [29], 3,2,3-tet [30] and tn [31] complexes. Furthermore, in the cyclam case, the trans isomer is the only product even when the reactant is cis [28]. Such cis→trans rearrangements may be advantageous in that the starting materials are often more accessible in the cis form, while trans systems are more interesting to study.

Isomer mixtures were separable by ion-exchange chromatography and/or selective precipitation. Complex cations were generally isolated as the perchlorates but in some case precipitation as the chlorides was convenient [28,30,35]. The trans salts are normally less soluble than the cis. In the case of *trans*- and *cis*-$[Cr(NH_3)_4(CN)_2]ClO_4$, the solubilities in water are different enough to allow complete isomer separation [23].

The only known tricyanoamine, $Cr(tacn)(CN)_3$, was also synthesized in dmso by metathesis of $Cr(tacn)(dmso)_3^{3+}$, which in turn was prepared in situ by previous heating of dissolved $Cr(tacn)Br_3$ [36], $Cr(tacn)Cl_3$ [32] or $Cr(tacn)(OSO_2CF_3)_3$ [32].

This class of reaction includes the preparation of $[(CN)(tmpa)Cr(\mu\text{-}O)\text{-}Cr(tmpa)(CN)](ClO_4)_2 \cdot 2H_2O$ by displacement of a single hydroxo bridge from $(tmpa)Cr(\mu\text{-}OH)_2Cr(tmpa)^{4+}$ in CH_3CN solution [37].

2.3 CN^- anation of Cr(III)-ammines in methanol suspension

Heterogeneous conditions may prove advantageous where solution chemistry fails to yield the desired products. The latter need to be more insoluble than the reagents in the suspending media, so that precipitation protects them from further ligand substitution. The preparations are stereoretentive in that trans reagents give rise to trans products. The best results are attained by prolonged stirring of mixtures not far from room temperature.

Reaction of a CH_3OH slurry of *trans*-$[Cr(NH_3)_4(dmso)Cl](ClO_4)_2$ and excess NaCN led to the formation of *trans*-$Cr(NH_3)_4(CN)Cl^+$, which separated as the cyanide salt [38]. Similar procedures were used to prepare *trans*-$Cr(NH_3)_4(CN)(NCS)^+$ and *trans*-$Cr(NH_3)_4(CN)F^+$ from *trans*-$[Cr(NH_3)_4(H_2O)(CN)](ClO_4)_2$ and NH_4NCS or NH_4F [38].

Of particular importance is the recent finding that a second CN^- can be selectively coordinated to $Cr(NH_3)_5(CN)^{2+}$ salts suspended in methanol saturated with $LiClO_4$ to yield *trans*-$[Cr(NH_3)_4(CN)_2]ClO_4$ [39]. The trans-directing power of CN^- destabilizes a $Cr—NH_3$ bond, usually very stable and persistent throughout the substitution reactions of acido groups [1,6–9]. The same product was obtained even when the starting complex was $Cr(NH_3)_5(dmso)^{3+}$. Therefore, in addition to greatly simplifying the preparation of *trans*-$Cr(NH_3)_4(CN)_2^+$, this route provides a facile and efficient entry to the *trans*-tetraamminechromium(III) series, otherwise accessible through several laborious steps [1].

2.4 Reaction of Cr(III) salts with CN^- and amines

Dicyano species occasionally form in "one-pot" mixtures of soluble Cr(III) salts, cyanide and diamines. Treatment of an aqueous HCN solution of $CrCl_3 \cdot 6H_2O$

with excess en yielded *cis*-$Cr(en)_2(CN)_2^+$ [40]. This compound was also obtained by heating the same chloride salt with stoichiometric amounts of KCN and en in methanol solution [22].

The analogous *cis*-$Cr(pn)_2(CN)_2^+$ complex was synthesized from $[Cr(H_2O)_6]_2(SO_4)_3 \cdot nH_2O$, KCN and pn without any solvent and recovered as the chloride salt [41]. Immediate formation of $Cr(pn)_2(H_2O)_2^{3+}$ was followed by slower entry of CN^-. The $Cr(pn)(CN)_4^-$ anion was subsequently isolated from the same reaction mixture by ion-exchange techniques and precipitated as the Mg^{2+} or Na^+ salt [42].

2.5 *Aquation of Cr(III)-cyanoam(m)ines*

Several cyanoaquoam(m)ines have been described as products of either cyanide or am(m)ine aquation of dicyanoam(m)ine complexes. Cyanide loss is a typical thermal reaction, whereas am(m)ine loss can be promoted photochemically.

Aquation of CN^- is a stepwise, acid-catalyzed, stereoretentive process: appropriate pH conditions allow accumulation of substantial amounts of first-step products. Pure *trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$ [23,39], *cis*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$ [23] and *cis*-$Cr(en)_2(H_2O)(CN)^{2+}$ [40] were obtained from the respective dicyano isomers. These dipositive ions were separated chromatographically from the monopositive reactants and the tripositive diaquo end products. Such a procedure was not necessary in the *trans*-tetraammine system, as accrual of the cyanoaquo ion was favoured by a thousandfold difference between the rates for the two aquation stages [23].

The conjugate bases *trans*- and *cis*-$Cr(NH_3)_4(OH)(CN)^+$ [23], as well as *cis*-$Cr(en)_2(OH)(CN)^+$ [40], were reversibly formed in alkaline solutions of the above complexes. Their higher resistance to decomposition compared with most Cr(III) hydroxo species, enabled quantification of the acidity of coordinated H_2O (vide infra) [23].

Thermally inaccessible $Cr(NH_3)_3(H_2O)(CN)_2^+$ ions are the major photoaquation products of *trans*- [43] and *cis*-$Cr(NH_3)_4(CN)_2^+$ [44] (vide infra). There are three such isomers: 1,6-CN-2-H_2O, 1,2-CN-6-H_2O and 1,2-CN-3-H_2O, labelled trans-mer, cis-mer and cis-fac, respectively, in relation to the trans or cis arrangements of the CN^- ligands. Photolyses are stereospecific in that these isomers are only produced two at a time: photoaquation of the trans system yielded mixtures of the two mer compounds [43], while in the cis system only the two cis forms were photogenerated [44]. The three configurations were inferred from the elution behaviour (dependent on the trans or cis position of the CN^- groups), combined with the mer or fac geometries of the $Cr(NH_3)_3(H_2O)_3^{3+}$ products of stereoretentive thermal aquation of cyanide.

The high solubility usually prevented isolation of the cyanoaquo complexes as solids; only for *trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$ was precipitation possible as the chloride and perchlorate salts [39].

2.6 Reaction of Cr(III)-cyano complexes with am(m)ines

The conceivably simplest route to anionic species, am(m)ine coordination to CN^--containing compounds, has not been fully explored and to date has only been followed to prepare $Cr(NH_3)(CN)_5^{2-}$. Obstacles to this method appear to be the inertness of $Cr(CN)_6^{3-}$ and the reaction cascades that follow displacement of one CN^- and result in mixtures with low amounts, if any, of the desired product.

These difficulties were circumvented by the selectivity of photosubstitution. Narrow-band irradiation of a CH_3OH solution of $(Ph_4P)_3[Cr(CN)_6]$ cleanly led to $Cr(CH_3OH)(CN)_5^{2-}$, which quantitatively turned into $Cr(NH_3)(CN)_5^{2-}$ by reaction with NH_3 dissolved in the same medium [45]. The advantages of methanol are (1) the low coordinating power that allows ready replacement by other ligands, (2) the capability to dissolve large concentrations of NH_3, and (3) easy elimination for product recovery.

2.7 NC bridging of Cr(III)-a(m)mines in the solid state

Heating of salts consisting of *trans*-$Cr(NN)_2(H_2O)F^{2+}$ cations and $M(CN)_4^{2-}$ or $M(CN)_6^{3-}$ anions, causes loss of the volatile H_2O ligands and formation of Cr—NC—M links. In this manner, Ribas et al. have synthesized numerous dinuclear complexes of general formulae $F(NN)_2Cr(\mu\text{-}NC)M(CN)_3$ and $F(NN)_2Cr(\mu\ NC)M(CN)_5^-$, where NN = en [46–50], tn [48–50], and M = Ni(II) [46,48], Pd(II) [48], Pt(II) [48], Co(III) [47,49], Cr(III) [50]. Using cyano-nitrosyl precursors, they have similarly prepared $F(NN)_2Cr(\mu\text{-}NC)Cr(NO)(CN)_4^-$ (NN = en, tn) [50] and $F(NN)_2Cr(\mu\text{-}NC)Fe(NO)(CN)_4$ (NN = tn, chxn) [51].

Mixed-diamine species such as $F(en)(tn)Cr(\mu\text{-}NC)Pt(CN)_3$ and $F(chxn)(tn)Cr(\mu\text{-}NC)Pt(CN)_3$ have also been obtained [52].

Dehydration–anation appears to take place with trans→cis isomerization about the Cr centre, with the exception of NN = tn and M = Ni, Pd, Pt [48]. In several cases, activation parameters were determined by thermogravimetry and differential scanning calorimetry: the reaction mechanism was proposed to involve a square-pyramidal Cr(III) intermediate and elimination of H_2O as Frenkel defects [49,51,53]. Undefined tri- and polynuclear compounds may accompany formation of $F(NN)_2Cr(\mu\text{-}NC)Cr(CN)_5^-$ (NN = en, tn) [54].

This technique cannot be utilized to obtain complexes of the type $(NH_3)_5Cr(\mu\text{-}NC)M(CN)_5$ starting from $[Cr(NH_3)_5(H_2O)][M(CN)_6]$ salts in spite of its success with the Co(III) analogues [18]. Detailed thermal studies have shown NH_3 evolution to precede H_2O evolution, in line with the greater lability of the Cr—NH_3 bond compared with the Co—NH_3 bond and the higher affinity of Cr(III) for oxygen. The complexes decompose gradually in a complicated way, without formation of uniform products [55,56]. There is IR evidence for CN bridging in the final polymers of composition $Cr(NC)_6M$ [55]. $[Cr(NH_3)_6][M(CN)_6]$ compounds were reported to behave similarly [56].

This notwithstanding, the Cr(III)–Fe(II) anion $(NH_3)_5Cr(\mu\text{-}NC)Fe(CN)_5^-$ was obtained by moderate heating (60°C) of $[Cr(NH_3)_5(H_2O)]_4[Fe(CN)_6]_3$ [57].

By an even milder procedure, the *cis*-$[Cr(en)_2(H_2O)X][M(CN)_4]$ solids with X = Cl, Br, and M = Ni, Pd, Pt, were converted into *cis*-$X(en)_2Cr(\mu\text{-}NC)M(CN)_3$ on standing in a desiccator for several days at room temperature [58].

2.8 NC and CN bridging of Cr(III)-am(m)ines in solution

This alternative is especially convenient where solid-phase treatments are unsuccessful. Cr(III)-aquoam(m)ine cations are usually anated by cyano complexes in water under moderate conditions; the products are then recovered by addition of organic solvents or precipitating agents, often following chromatographic purification.

$Cr(NH_3)_5(H_2O)^{3+}$ reacts with $Co(CN)_6^{3-}$ in aqueous medium to give $(NH_3)_5Cr(\mu\text{-}NC)Co(CN)_5$ [59]. Similar reaction with $Fe(NO)(CN)_5^{2-}$ yields $(NH_3)_5Cr(\mu\text{-}NC)Fe(NO)(CN)_4^+$ [60].

A variety of dinuclear complexes with Cr(III)-diamines has been thus obtained: *cis*-$X(en)_2Cr(\mu\text{-}NC)M(CN)_3$ (X = Cl, Br; M = Ni [46], Pd, Pt [58]), *cis*-$F(en)_2Cr(\mu\text{-}NC)M(CN)_5^-$ (M = Cr [47,54], Co [47]), *cis*-$F(pn)_2Cr(\mu\text{-}NC)M(CN)_3$ (M = Ni, Pd, Pt), *cis*-$F(pn)_2Cr(\mu\text{-}NC)M(CN)_5^-$ (M = Cr, Co), *cis*-$F(pn)_2Cr(\mu\text{-}NC)Cr(NO)(CN)_4^-$ [61], and *trans*-$F(tn)_2Cr(\mu\text{-}NC)Cr(CN)_5^-$ [54]. The original cis or trans geometry of the $Cr(NN)_2(H_2O)X^{2+}$ components is retained when X = Cl or Br [46,58] and NN = tn [54], whereas the systems with X = F and NN = en or pn [47,61] undergo trans → cis rearrangement, as in the solid-state anation.

Photolysis of aqeous $\{Cr(en)_3^{3+}; Fe(CN)_6^{4-}\}$ ion pairs upon ligand-field excitation of Cr(III) was found to give rise to $(H_2O)(en)_2Cr(\mu\text{-}NC)Fe(CN)_5^-$, which was isolated as the Ph_4As^+ salt. The Cr(III)–Ru(II) and Cr(III)–Os(II) homologues were spectrally detected in photolyzed solutions but could not be precipitated [62].

Non-aqueous media have also been employed for cyanide bridging. The Cr(III)–Ru(II) 2:1 trinuclear cation $[(NH_3)_5Cr(\mu\text{-}NC)]_2Ru(bpy)_2^{6+}$ was obtained in acetone from $Cr(NH_3)_5(OSO_2CF_3)^{2+}$ and $Ru(bpy)_2(CN)_2$, while it was not possible to isolate pure samples of the 1:1 ion $(NH_3)_5Cr(\mu\text{-}NC)Ru(bpy)_2(CN)^{3+}$ [63]. Reaction of the same Cr species with $Co(NH_3)_5(CN)^{2+}$ in sulpholane gave $(NH_3)_5Cr(\mu\text{-}NC)Co(NH_3)_5^{5+}$ [64].

A few compounds have been reported where the cyano bridge is C-bonded to a Cr(III)-am(m)ine. The $(NH_3)_5Cr(\mu\text{-}CN)Cr(NH_3)_5^{5+}$ homodinuclear ion was prepared in sulpholane by condensing $Cr(NH_3)_5(CN)^{2+}$ with $Cr(NH_3)_5(OSO_2CF_3)^{2+}$ [64]. A second Cr–CN–Cr species, *trans*-$(NC)(cyclam)Cr(\mu\text{-}CN)Cr(CN)_5^-$, was synthesized in methanol from *trans*-$Cr(cyclam)(CN)_2^+$ and $Cr(CN)_5(dmf)^{2-}$ photogenerated from $Cr(CN)_6^{3-}$ in dmf [65]. Analogous interaction with $Ru(bpy)_2Cl_2$ in water yielded the heterotrinuclear $[trans\text{-(NC)(cyclam)Cr}(\mu\text{-CN})]_2\text{Ru(bpy)}_2^{4+}$ complex [66].

3. STRUCTURAL PROPERTIES

3.1 Crystallographic studies

The ligand arrangement of some mono- and polynuclear Cr(III)-cyanoam(m)ines has been elucidated by X-ray diffraction techniques.

Trans-$[\text{Cr(cyclam)(CN)}_2]\text{ClO}_4$ was shown to crystallize in the orthorhombic system and its cyclam moiety to have a chair conformation. The study proved the chemically interesting feature of this complex, i.e. the rigid, virtually coplanar assembly of the amine N atoms and the Cr ion. Only a slight departure from the octahedral geometry resulted from 1.3° and 1.9° deviations of the CN^- groups from the normal to the equatorial plane [67].

In *cis*-$[\text{Cr(tet}b\text{)(CN)}_2]\text{Cl}$, the hexamethylated derivative of the cyclam ring exerts its propensity for formation of cis complexes due to the "folding" conformation of the geminal CH_3 groups in the 7 and 14 positions. The orthorhombic crystals show longer Cr—N bonds and smaller N—Cr—N angles than in analogous trans species, denoting a more strained coordination [68].

Structural differences and Λ absolute configurations were determined for two of the three possible geometric isomers of $(-)_D$-*cis*-$[\text{Cr}(d\text{-pn})_2(\text{CN})_2]\text{Cl}$, both forming orthorhombic unit cells. The N—Cr—N angles of the chelate rings range between 81.4° and 83.1°, and are comparable with those of Cr—en complexes [69].

$\text{Cr—CN} \rightarrow \text{Cr—NC}$ linkage isomerization was demonstrated by analysis of the monoclinic crystals of Δ-*cis*-$[\text{Cr(en)}_2(\text{NCAgCN})_2]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$, recovered from solutions of optically active *cis*-$\text{Cr(en)}_2(\text{CN})_2^+$ in the presence of AgClO_4. The Cr—N—C—Ag assemblies were established to be nearly linear [70].

The crystal system of $[(\text{NH}_3)_5\text{Cr}(\mu\text{-NC})\text{Fe(NO)(CN)}_4]\text{ClO}_4 \cdot 3\text{H}_2\text{O}$ was found to be hexagonal and the molecular structure to involve an unusually large distortion (−51.3°) in the Cr—N—C—Fe torsion angle, proposed to arise from interaction with the NO ligand cis to the cyano bridge [60].

$\{[trans\text{-(NC)(cyclam)Cr}(\mu\text{-CN})]_2\text{Ru(bpy)}_2\}(\text{PF}_6)_4$ is one of the very few trinuclear compounds for which a crystal structure was obtained. This confirmed the CN^- groups to be trans about each Cr centre and the Ru component to have a cis configuration, with non-linear Ru—N—C—Cr chains bent away from each other [71].

3.2 Optical activity

Resolution into optical isomers has been particularly useful to distinguish bischelated *cis*-$\text{Cr(NN)}_2(\text{CN})_2^+$ species from their trans counterparts, as no clue in this regard is offered by absorption spectra (vide infra). The two enantiomers of *cis*-Cr(en)$_2$(CN)$_2^+$ were separated by precipitation of the (+)$_D$ form with (+)$_D$-bcs [35,40,42].

In *cis*-Cr(pn)$_2$(CN)$_2^+$, the diamine itself is chiral; combination of chromatography and diastereomer formation with (+)$_D$- and (−)$_D$-bcs enabled isolation of (−)$_D$-*cis*-Cr(*d*-pn)$_2$(CN)$_2^+$, (+)$_D$-*cis*-Cr(*l*-pn)$_2$(CN)$_2^+$, (+)$_D$- and (−)$_D$-*cis*-Cr(*d*-pn)(*l*-pn)(CN)$_2^+$ [41]. Molar rotations and circular dichroism (CD) data of the resolved compounds are assembled in Table 2.

The absolute configurations of the above complexes, as well as those of (+)$_D$-Cr(*d*-pn)$_3^{3+}$ and (−)$_D$-Cr(*l*-pn)$_3^{3+}$, were collectively determined [42] by CD comparison with Λ-(−)$_D$-*cis*-Cr(*d*-pn)$_2$(CN)$_2^+$ [69] and Λ-(+)$_D$-Cr(en)$_3^{3+}$ [72], the configurations of which had been authenticated crystallographically. The assignments are included in Table 2. In an earlier study, the opposite attribution was tentatively made for the Cr(en)$_2$(CN)$_2^+$ isomers, based on arguments relating the Co(III) analogues [40].

The contribution of the localized chirality of a single pn ligand to the CD spectra was ascertained through the Cr(*d*-pn)(CN)$_4^-$ and Cr(*l*-pn)(CN)$_4^-$ anions, non-chiral around the Cr centre, so as to interpret correctly the results for bis- and trischelated systems [42].

It is noteworthy that separation of the three conformational isomers of Λ-(−)$_D$-*cis*-Cr(*d*-pn)$_2$(CN)$_2^+$ resulting from different relative positions of the pn methyl groups was achieved by chromatographic chiral interaction with Sb$_2$(μ-*d*-tartrato)$_2^{2-}$. As already mentioned [69], two of these species yielded X-ray quality crystals.

3.3 Infrared spectra

Rather than reporting a frequency tabulation, the IR features regarded as most significant from a structural standpoint are selectively considered.

The CN stretching of Cr(NH$_3$)$_5$(CN)$^{2+}$ [27], Cr(NH$_3$)$_4$(CN)$_2^+$ [23] and Cr(NN)$_2$(CN)$_2^+$ complexes [21,26,31,40,69,73] is generally associated with a very weak single peak at 2130–2140 cm^{-1}. The low intensity, compared with that of similar Co(III) species, was ascribed to M—CN π-bonding differences [21]. The band conveys no stereochemical information: for example, in apparent inconsistency with the symmetries, a small splitting occurs in *trans*-Cr(NH$_3$)$_4$(CN)$_2^+$, but not in its cis isomer [23].

The frequency lowering in the *trans*-CrN$_4$(CN)$_2^+$ ions with N$_4$ = cyclam (2090 cm^{-1}) [28] and tet*a* (2080 cm^{-1}) [29], was taken to indicate a better π-acceptance of CN$^-$, consistent with the macrocycles being stronger σ donors than other am(m)ines. A well-defined asymmetric doublet at 2136–2143 cm^{-1} proved useful in characterizing Cr(phen)(CN)$_4^-$ [26].

A proposed criterion for geometric discrimination of bis-en compounds is the number of bands in the 395–550 cm^{-1} region: four in the case of cis isomers and

TABLE 2

Optical activity

Complex	Salt	[M][a]	CD peaks		Absolute configuration	Ref.
			λ (nm)	$\Delta\varepsilon$[b]		
$(+)_D$-*cis*-$Cr(en)_2(CN)_2^+$	Cl^-		429	+0.51		21
			335	−0.036		
	Cl^-	+103.2				35
		+190.8[c]				
	ClO_4^-	+94.8				
		+175.7[c]				
	I^-	+101	424	+0.42[d]		40
			334	−0.03[d]		
	Cl^-		429	+0.494	Λ	42
			336	−0.044		
$(-)_D$-*cis*-$Cr(en)_2(CN)_2^+$	I^-	−98.5	424	−0.37[d]		40
			334	+0.03[d]		
	Cl^-		429	−0.495	Δ	41
			336	+0.04[d]		
$(-)_D$-*cis*-$Cr(d\text{-}pn)_2(CN)_2^+$ (A)[e]	Cl^-	−171.6	459	+0.484	Λ	69
			413	−0.196		
			352	+0.040		
(B)[e]	Cl^-	−157.9	458	+0.445	Λ	69
			413	−0.191		
			351	+0.053		
(C)[e]	Cl^-	−138.4	457	+0.400	Λ	69
			413	−0.181		
			352	+0.054		
$(+)_D$-*cis*-$Cr(l\text{-}pn)_2(CN)_2^+$	Cl^-	+168[f]	457	−0.557	Δ	42
			413	+0.219		
			353	−0.059		
$(+)_D$-*cis*-$Cr(d\text{-}pn)(l\text{-}pn)(CN)_2^+$	Cl^-	+103[f]	425	+0.580	Λ	42
			338	−0.045		
$(-)_D$-*cis*-$Cr(d\text{-}pn)(l\text{-}pn)(CN)_2^+$	Cl^-	−105[f]	425	−0.573	Δ	42
			338	+0.050		
$Cr(d\text{-}pn)(CN)_4^-$	Mg^{2+}		441	+0.075		42
			392	−0.384		
			310	+0.052		
$Cr(l\text{-}pn)(CN)_4^-$	Na^+		442	−0.081		42
			394	+0.383		
			331	−0.059		

---

[a] Molar rotation, deg(mol/100 cm^3)$^{-1}$ dm^{-1}, at 589 nm (Na$_D$), unless otherwise noted; temperature 15–25°C.

[b] $(\varepsilon_L - \varepsilon_R)$ M^{-1} cm^{-1}.

[c] 546 nm.

[d] Taken from graphs in cited references.

[e] Geometric isomers resulting from different relative positions of the methyl groups; see Fig. 1 of ref. 69.

[f] Evaluated from specific rotations of ref. 41.

three for trans isomers [74], although the reliability of the method has been questioned since anion effects have occasionally been found to increase this number [75]. The rule, however, appeared applicable to the chloride [21], iodide [40] and perchlorate [34] salts of $Cr(en)_2(CN)_2^+$ and was extensible to $[Cr(tn)_2(CN)_2]ClO_4$ [31].

Also cyclam complexes can usually be distinguished by their 790–910 cm^{-1} patterns arising from amine and methylene vibrations, the cis forms showing more splitting than the trans [76]. The 800 cm^{-1} singlet and the 873–882 cm^{-1} doublet thus supported the trans assignment of $Cr(cyclam)(CN)_2^+$ [28].

Cyano-bridge formation between metal centres is accompanied by a splitting of the CN stretching band into two distinct peaks, one invariant with respect to the mononuclear species and the other shifted by 30–50 cm^{-1} toward higher energies. The former still denotes terminal CN^- ligands while the latter, seen in most cases around 2160–2180 cm^{-1}, is assigned to vibrations of bridging cyanide. Such frequencies have been measured for a variety of Cr—NC—M dinuclear compounds, where M = Cr [47,50,54,61], Fe [51,60], Co [47,59,61], Ni [46,48,58,61], Pd and Pt [48,52,58,61]. In agreement with this trend, the trinuclear Cr—CN—Ru—NC—Cr complex mentioned above exhibits a band at 2133 cm^{-1} [66], to be compared with the 2090 cm^{-1} band in the free *trans*-$Cr(cyclam)(CN)_2^+$ unit [28].

3.4 *Magnetic behaviour of homodinuclear complexes*

The magnetic moments of mononuclear Cr(III)-acidoam(m)ines are in the 3.5–4.1 B.M. range, close to the calculated "spin-only" value of 3.87 B.M. for a d^3 system [1]. Antiferromagnetic exchange interactions between the Cr atoms of dinuclear complexes can lower such a value [5].

The temperature dependence of the magnetic moment of $[(CN)(tmpa)Cr(\mu\text{-}O)Cr(tmpa)(CN)](ClO_4)_2 \cdot 2H_2O$ between 6 and 300 K was indicative of strong antiferromagnetic coupling. The data were fit with a relatively large coupling parameter, $J = -290\ cm^{-1}$ (in the interaction Hamiltonian $H = -2JS_1S_2$) [37]. The observed diamagnetic ground state is consistent with the interaction being mediated by $d_\pi(Cr)$–$p_\pi(O)$ orbital overlaps, as is the case for other linear oxo-bridged dimers [17].

Cyano-bridged systems exhibit a much weaker spin coupling, as the π interaction extends through three bonds, compared with two bonds in the oxo-bridged systems. Magnetic susceptibility variations of $[(NH_3)_5Cr(\mu\text{-}CN)Cr(NH_3)_5](ClO_4)_5 \cdot 4H_2O$ in the 4–300 K range gave $J = -16.2\ cm^{-1}$. The quintet and septet states of this complex were identified by EPR spectra: the J values derived from the latter agreed well with the susceptibility results [64].

The magnetic behaviour was also investigated in various salts of *cis*-$F(NN)_2Cr(\mu\text{-}NC)Cr(CN)_5^-$ with NN = en or tn [50,54]; different J values of ca. −1.5 [50] and ca. −20 cm^{-1} [54] were reported, however.

No magnetic exchange was detected between the Cr(III) and Cr(I) centres of *cis*-$K[F(en)_2Cr(\mu\text{-}NC)Cr(NO)(CN)_4]$ [50].

4. ELECTRONIC SPECTRA

4.1 Ligand-field quartet absorption

The UV-visible spectra are listed in Table 3 according to increasing number of coordinated CN^- groups, i.e. increasing overall ligand-field (LF) strength. Such features of relatively low intensity arise from spin-allowed, but Laporte-forbidden, d–d electron excitations and are well accounted for by LF theory [4]. Cr(III) complexes have received particular attention in this regard [2–4]. The two bands typically observed in these d^3 systems are associated with the $^4A_2 \rightarrow {}^4T_2$ and $^4A_2 \rightarrow {}^4T_1(F)$ transitions in octahedral approximation (where the parity notation g is omitted) and in order of increasing energy. A third LF band, predicted at shorter wavelengths for $^4A_2 \rightarrow {}^4T_1(P)$, is obscured in all am(m)ine species by the more intense charge-transfer (CT) absorptions.

In the actual symmetries of the acidoam(m)ines the $^4T_2$ and $^4T_1$ excited states split. Decomposition into the respective $^4E + {}^4B_2$ and $^4A_2 + {}^4E$ sublevels is most common, as it pertains to CrN_5X (C_{4v}), *trans*-CrN_4X_2 (D_{4h}) and *trans*-CrN_4XY (C_{4v}) compounds. Even *cis*-CrN_4X_2 ions, of strict C_{2v} local symmetry (which generates a larger number of components), can be treated as approximately D_{4h} with energy spacings that are half of those for the trans isomers [3]. The tetragonal splittings are related to either the global LF parameters Dt and Ds [3], or the angular overlap model (AOM) ligand parameters σ_L and π_L [4,13], whose advantage is the individual "chemical" significance.

Cyanoam(m)ines are electronically atypical among acidoam(m)ines, due to the higher spectrochemical strength of CN^- relative to am(m)ines, in contrast with the lower spectrochemical position of all other acido groups. The splittings, which are determined by the difference between axial and equatorial field-strengths, are thus opposite to the usual occurrence and give rise to different energy-level sequences [3]. For *trans*-$CrN_4(CN)_2^+$, the lowest excited state is $^4B_2$ rather than ^4E; analogously, for *cis*-$CrN_4(CN)_2^+$, such a state is ^4E instead of $^4B_2$. These inversions are particularly relevant to photochemistry.

Since CN^- and am(m)ines are not spectrochemically far apart, there is little evidence of band splitting, so that the LF spectra are poorly diagnostic as to trans/cis assignment. The extinction coefficients are expectedly higher for cis than for trans systems, and tend to increase with the complexity of the N-bound ligands.

It is noteworthy that for $Cr(NH_3)_5(CN)^{2+}$ [27], $Cr(NH_3)(CN)_5^{2-}$ [45], as well as for *trans*- and *cis*-$Cr(NH_3)_4(CN)_2^+$ [23], the LF spectra were anticipated with fair accuracy [3] long before these complexes were actually synthesized.

TABLE 3

Ligand-field absorption data (nm) of mononuclear complexes in various solvents (molar extinction coefficients, $M^{-1}\ cm^{-1}$, in parentheses)

Complex	Solvent	λ_{max}	λ_{min}	λ_{max}	Ref.
$Cr(NH_3)_5(CN)^{2+}$	H_2O[c]	451 (42.6)	391 (10.0)	347 (37.7)	27
	dmso	452 (45)	392 (11)[a]	348 (40)[a]	78
	dmf	453 (45)	393 (11)[a]	348 (40)[a]	78
	tms	454 (46)	393 (13)[a]	348 (41)[a]	78
$Cr(ND_3)_5(CN)^{2+}$	D_2O	451 (40.0)	391 (8.0)[a]	347 (35)[a]	78
trans-$Cr(NH_3)_4(H_2O)(CN)^{2+}$	H_2O[c]	468 (48.0)	400 (10.0)	354 (32.2)	23
trans-$Cr(NH_3)_4(OH)(CN)^+$	H_2O[d]	494 (55)	426 (21)	381 (39)	23
trans-$Cr(NH_3)_4(NCS)(CN)^+$	H_2O[c]	466 (81.9)	401 (18.3)[a]	355 (51,sh)	77
	dmso	468 (82)	402 (18)[a]	357 (50)	38
	dmf	468 (80)	402 (18)[a]	357 (48)	38
trans-$Cr(NH_3)_4Cl(CN)^+$	H_2O[c]	488 (51.5)	419 (13.1)[a]	368 (40.0)	38
	dmso	490 (51)	421 (13)[a]	371 (41)	38
	dmf	490 (54)	422 (14)[a]	370 (41)	38
trans-$Cr(NH_3)_4F(CN)^+$	H_2O[c]	483 (59.5)	410 (10.6)[a]	355 (21.8)	77
	dmso	495 (60)	419 (12)[a]	386 (17)[e]	38
	dmf	496 (61)	420 (12)[a]	388 (16)[f]	38
cis-$Cr(NH_3)_4(H_2O)(CN)^{2+}$	H_2O[c]	468 (34)	400 (11)	355 (32)	23
cis-$Cr(NH_3)_4(OH)(CN)^+$	H_2O[d]	491 (46)	432 (25)	387 (44)	23
cis-$Cr(NH_3)_4(dmso)(CN)^{2+}$	H_2O[c]	483 (44)	406 (13)	362 (36)	23
cis-$Cr(en)_2(H_2O)(CN)^{2+}$	H_2O[g]	467 (53.4)	399 (21)[b]	356 (49.1)	40
cis-$Cr(en)_2(OH)(CN)^+$	H_2O[h]	488 (59.4)		386 (54.5)	40
trans-$Cr(NH_3)_4(CN)_2^+$	H_2O[c]	440 (42.6)	385 (12.5)	344 (41.5)	23
	dmso	443 (45)	389 (14)[a]	345 (44)[a]	78
	dmf	444 (46)	390 (16)[a]	344 (45)[a]	78
mer-1,6-CN-$Cr(NH_3)_3(H_2O)(CN)_2^+$	H_2O[c]	449 (39)	395 (19)	351 (41)	43
mer-1,2-CN-$Cr(NH_3)_3(H_2O)(CN)_2^+$	H_2O[c]	452 (53)	391 (17)	350 (34)	43
fac-$Cr(NH_3)_3(H_2O)(CN)_2^+$	H_2O[c]	445 (44)	388 (19)	350 (37)	44
trans-$Cr(en)_2(CN)_2^+$	H_2O	432 (49.0)	377 (14)[b]	337 (42.7)	21
	H_2O	433 (50.1)		337 (42.7)	22
trans-$Cr(tn)_2(CN)_2^+$	H_2O[c]	441 (52.5)	385 (14)[b]	344 (47.5)	31
trans-$Cr(3,2,3\text{-}tet)(CN)_2^+$	H_2O	440 (71.2)	383 (18.2)	343 (65.4)	*m*
trans-$Cr(cyclam)(CN)_2^+$	H_2O	414 (62.5)	365 (22)	328 (62.5)	28
trans-Cr(tet*a*)$(CN)_2^+$	H_2O	425 (67.8)		366 (70.0)	29
	H_2O	426 (63)		337 (59)	32
trans-$Cr([15]aneN_4)(CN)_2^+$	H_2O	452		348	68
cis-$Cr(NH_3)_4(CN)_2^+$	H_2O[c]	436 (49.0)	379 (14.0)	342 (37.6)	23
	dmso	441 (46)	384 (15)[a]	343 (39)[a]	78
	dmf	441 (48)	384 (16)[a]	343 (39)[a]	78
	tms	440 (44)	385 (15)[a]	344 (39)[a]	78
cis-$Cr(en)_2(CN)_2^+$	H_2O	433 (70.8)	378 (21)[b]	339 (63.1)	21
	H_2O	434 (70.0)	378 (21)[b]	339 (62.3)	40
	H_2O	434 (69.5)		339 (62.2)	22
	H_2O	436 (69)		342 (63)	42

TABLE 3 *continued*

Complex	Solvent	λ_{max}	λ_{min}	λ_{max}	Ref.
cis-$Cr(d\text{-pn})_2(CN)_2^+$	H_2O	435 (76)	377 (26)[b]	339 (68)	42
cis-$Cr(l\text{-pn})_2(CN)_2^+$	H_2O	435 (76)		339 (68)	42
cis-$Cr(d\text{-pn})(l\text{-pn})(CN)_2^+$	H_2O	433 (83)		339 (68)	42
cis-$Cr(tet\textit{b})(CN)_2^+$	H_2O	447 (112)[i]		347 (98)	32
	dmso	440			68
	CH_3CN	437			68
	acetone	432			68
cis-$Cr(bpy)_2(CN)_2^+$	dmso	420 (362,sh)[j]		395 (519,sh)	26
$Cr(edta)(H_2O)(CN)_2^{3-}$	H_2O[k]	512 (70.4)	450 (45.0)	386 (83.0)	25
$Cr(tacn)(CN)_3$	H_2O	421 (63)		334 (71)	32
	H_2O	420 (67)		332 (80)	36
$Cr(d\text{-pn})(CN)_4^-$	H_2O	404 (83)	358 (35)[b]	324 (71)	42
$Cr(l\text{-pn})(CN)_4^-$	H_2O	404 (79)		324 (63)	42
$Cr(phen)(CN)_4^-$	dmso	402 (87,sh)[l]		352 (1000)	26
$Cr(NH_3)(CN)_5^{2-}$	H_2O	397 (90)	348 (34)[a]	320 (54)	45
	dmso	406 (77)	355 (35)[a]	324 (58)	45
	dmf	406 (72)	356 (32)[a]	316 (66)	45

[a] P. Riccieri and E. Zinato, unpublished data.
[b] Estimated from figures in cited references.
[c] 10^{-3} M $HClO_4$.
[d] pH 10 (NaOH).
[e] Long-wavelength component of a split band: other maximum at 342 nm ($\varepsilon = 16$).
[f] Long-wavelength component of a split band: other maximum at 337 nm ($\varepsilon = 16$).
[g] pH 2.9, $\mu = 2.0$.
[h] pH 10.4, $\mu = 2.0$.
[i] Other maximum at 462 nm ($\varepsilon = 110$).
[j] Additional shoulder at 450 nm ($\varepsilon = 156$).
[k] pH 12.
[l] Additional shoulder at 416 nm ($\varepsilon = 82$).
[m] S. Kaizaki, private communication.

The *trans*-$Cr(NH_3)_4X(CN)^{z+}$ species with $X = H_2O, F^-, Cl^-$ and NCS^-, form a peculiar group, where the balancing of the spectrochemical strengths of CN^- and X, respectively higher and lower than that of NH_3, results in exiguous differences between axial and equatorial fields: these complexes are electronically quasi-octahedral, although their geometries are truly tetragonal [38,77].

Solvent effects on LF maxima and intensities are usually modest for cationic species [78]. On the other hand, the $Cr(NH_3)(CN)_5^{2-}$ anion appears to be rather sensitive to the change from aqueous to aprotic media. The higher transition energies in water have been attributed to tightening of the solvation shell by hydrogen bonding between CN^- and the H_2O molecules properly oriented towards a negative complex ion [45]. The marked spectral variation of the *trans*-$Cr(NH_3)_4F(CN)^+$

cation, comprising the splitting of the high-energy band into two distinct maxima, is ascribed to F^- interactions. For *trans*-$Cr(3,2,3\text{-tet})F_2^+$, such absorption shifts have been correlated with solvent acceptor numbers and with changes of the Cr—F σ-bond strength, as quantified by the AOM parameter σ_F [30].

In cyano-bridged homo- and heterodinuclear Cr(III)-am(m)ines, the monometallic units behave as virtually independent chromophores in that the LF absorptions generally match closely the sum of those for the separated components. In particular, LF maxima can distinguish between Cr—CN— and Cr—NC— bridging. The latter moiety, unstable in a mononuclear context, is spectroscopically comparable with the $Cr—NH_3$ moiety, and involves a 10–15 nm blue shift of the low-energy LF band upon replacement of an H_2O ligand by the NC bridge. Table 4 reports representative data for systems having a small spectral overlap between the subunits in this region.

4.2 Ligand-field doublet absorption

The lowest-energy spin-forbidden transition of $^4A_2 \rightarrow {}^2E$ octahedral parentage, has been measured in few cases [21,40,54,64,78]. It appears as a series of very weak

TABLE 4

Lowest-energy ligand-field absorption maxima of the Cr(III)-am(m)ine moieties of isocyano-bridged dinuclear complexes in aqueous solution

Cr moiety	λ_{max}, nm	(ε, $M^{-1}\,cm^{-1}$)	Other fragment	Ref.
$(NH_3)_5Cr(NC)^{2+}$	468	(45)	$Co(CN)_5^{2-}$	59
	464	(55)	$Fe(NO)(CN)_4^-$	60
cis-$(en)_2Cr(NC)_2^+$	458	(79)	Ag^+[a]	73
$(H_2O)(en)_2Cr(NC)^{2+}$	498	(90)	$Ru(CN)_5^{3-}$	62
	493	(84)	$Os(CN)_5^{3-}$	62
cis-$F(en)_2Cr(NC)^+$	492	(84)	$M(CN)_3^-$[b]	48
	496	(36)	$Cr(CN)_5^{2-}$	50
	490/2	(50)	$Cr(CN)_5^{2-}$	54
	493		$Co(CN)_5^{2-}$	47
cis-$Cl(en)_2Cr(NC)^+$	501/2		$M(CN)_3^-$[b]	58
cis-$Br(en)_2Cr(NC)^+$	508/10		$M(CN)_3^-$[b]	58
cis-$F(tn)_2Cr(NC)^+$	502	(41)	$Cr(CN)_5^{2-}$	50
	499	(43)	$Cr(CN)_5^{2-}$	54
	500		$Fe(NO)(CN)_4^-$	51
cis-$F(pn)_2Cr(NC)^+$	492/4	(60)	$M(CN)_3^-$[b]	61
	492/4	(60)	$M(CN)_5^{2-}$[c]	61
cis-$F(chxn)_2Cr(NC)^+$	495		$Fe(NO)(CN)_4^-$	51
cis-$F(en)(tn)Cr(NC)^+$	490		$Pt(CN)_3^-$	52
cis-$F(chxn)(tn)Cr(NC)^+$	495		$Pt(CN)_3^-$	52

[a] Silver adduct of *cis*-$Cr(en)_2(CN)_2^+$.
[b] M = Ni, Pd, Pt.
[c] M = Cr, Co.

($\varepsilon < 0.2$) and narrow details on the long-wavelength side of the first quartet band. The excitation promotes only spin pairing within the t_2^3 configuration, and the structure is indicative of vibronic coupling [2]. The available information is presented in Table 5. The low-energy features (not always sufficiently evident), are associated with the 0–0 transition: their positions are close to the $^2E \rightarrow {}^4A_2$ emission peaks (Table 6). Where investigated, solvent effects were found to be minimal for these transitions also [78]. In dinuclear complexes, these bands are apparently intensified by Cr—Cr exchange interactions [54,64].

4.3 *Emission*

Luminescence in low-temperature glassy matrices is typical of Cr(III) [15]. In ambient-temperature solution, the phenomenon is not so general: the cyanoam(m)ines therefore stand out because of their relatively strong emission under such conditions.

For N- and C-coordination, the ^2E state lies definitely below $^4T_2$, so that the emission is invariably $^2E \rightarrow {}^4A_2$ phosphorescence [2,15]. Since this intraconfigurational transition involves states having nearly the same geometry, the bands are narrow and but little shifted with respect to the $^4A_2 \rightarrow {}^2E$ absorptions. Moreover, they often exhibit vibronic structure even in fluid media at room temperature. The

TABLE 5

Quartet–doublet absorption maxima in various solvents

Complex	Solvent	Wavelengths, nm				Ref.
$Cr(NH_3)_5(CN)^{2+}$	H_2O	679	669	658	637	78
	dmso	681	671	659	637	78
	dmf	680	670	659	637	78
	tms	680	669		638	78
$Cr(ND_3)_5(CN)^{2+}$	D_2O	678	668	657		78
trans-$Cr(NH_3)_4(CN)_2^+$	H_2O		680	669	646	78
	dmso		682	670	647	78
	dmf		681	670	646	78
cis-$Cr(NH_3)_4(CN)_2^+$	H_2O			669	654	78
	dmso		690	671	655	78
	dmf		688	671	655	78
cis-$Cr(en)_2(CN)_2^+$	H_2O	702	684	666		21
	H_2O	702	683	665		40
$F(en)_2Cr(\mu\text{-}NC)Cr(CN)_5^-$	H_2O	677[a]				54
$F(tn)_2Cr(\mu\text{-}NC)Cr(CN)_5^-$	H_2O	677[a]				54
$(NH_3)_5Cr(\mu\text{-}NC)Cr(NH_3)_5^{5+}$	H_2O	660[b]				64

[a] $\varepsilon \approx 5\ M^{-1}\ cm^{-1}$.

[b] $\varepsilon = 1.8\ M^{-1}\ cm^{-1}$, estimated from graph in ref. 64.

TABLE 6

Emission maxima in various solvents[a]

Complex	Solvent	Wavelength, nm	Ref.
$Cr(NH_3)_5(CN)^{2+}$	H_2O[b]	680	78
	dmso	682	78
	dmf	682	78
	tms	682	78
$Cr(ND_3)_5(CN)^{2+}$	D_2O	680	78
trans-$Cr(NH_3)_4(H_2O)(CN)^{2+}$	H_2O[b]	688	77
trans-$Cr(NH_3)_4(NCS)(CN)^+$	H_2O[b]	709	77
	dmso	710	38
	dmf	709	38
trans-$Cr(NH_3)_4Cl(CN)^+$	H_2O[b]	697	82
	dmso	698	38
	dmf	699	38
trans-$Cr(NH_3)_4F(CN)^+$	H_2O[b]	685	77
	dmso	692	38
	dmf	691	38
cis-$Cr(NH_3)_4(H_2O)(CN)^{2+}$	H_2O[b]	685	78
cis-$Cr(NH_3)_4(dmso)(CN)^{2+}$	H_2O[b]	685	78
trans-$Cr(NH_3)_4(CN)_2^+$	H_2O[b]	700	78
	dmso	701	78
	dmf	699	78
trans-$Cr(en)_2(CN)_2^+$	$dmso/CF_3SO_3H$	703	34
trans-$Cr(tn)_2(CN)_2^+$	H_2O[b]	703	31
trans-$Cr(cyclam)(CN)_2^+$	H_2O[c]	720	83
	$dmso/H_2O$	716	68
trans-Cr(tet*a*)$(CN)_2^+$	H_2O[c]	715	29
	$dmso/H_2O$	715	68
trans-$Cr([15]aneN_4)(CN)_2^+$	$dmso/H_2O$	712	68
cis-$Cr(NH_3)_4(CN)_2^+$	H_2O[b]	701	78
	dmso	703	78
	dmf	702	78
	tms	702	78
cis-$Cr(en)_2(CN)_2^+$	$dmso/CF_3SO_3H$	705	34
cis-Cr(tet*b*)$(CN)_2^+$	$dmso/H_2O$[d]	725	32
cis-$Cr(bpy)_2(CN)_2^+$	$dmso/H_2O$[d]	756	26
$Cr(tacn)(CN)_3$	H_2O	742	36
	$dmso/H_2O$[d]	751	32
$Cr(phen)(CN)_4^-$	$dmso/H_2O$[d]	784	26
$Cr(NH_3)(CN)_5^{2-}$	dmso	777	45
	dmf	777	45
$(NH_3)_5Cr(\mu\text{-}NC)Co(CN)_5$[e]	H_2O[f]	685	59
$[(NH_3)_5Cr(\mu\text{-}NC)]_2Ru(bpy)_2^{6+}$[e]	$dmso/H_2O$[d]	680	63
$[(NC)(cyclam)Cr(\mu\text{-}CN)]_2Ru(bpy)_2^{4+}$[e]	H_2O	727	66
$(NC)(cyclam)Cr(\mu\text{-}CN)Cr(CN)_5^-$	dmf	778	65

[a] Data for room temperature of 20–25°C, unless otherwise noted.

[b] pH 3.0–3.3 ($HClO_4$).

[c] pH 2.3 (HNO_3).

[d] Glassy solution at 77 K.

[e] Emission from the Cr(III) unit.

[f] pH 1.7 ($HClO_4$).

prominent peaks are collected in Table 6. Where not available at 20–25°C, the data refer to 77 K glasses.

The ^2E octahedral level is rather insensitive to field strength and symmetry descent, but may be modified by the nephelauxetic effect of the ligands [2,4,15]. This is particularly important for CN^-, as delocalization of the t_2(Cr) electrons into the empty π^*(CN) orbitals lowers the energy of the ^2E state by reducing the repulsive interactions. While the phosphorescence of $Cr(NH_3)_6^{3+}$ and several acidoam(m)ines occurs at 650–680 nm, that of $Cr(CN)_6^{3-}$ is centred at ca. 800 nm [15,79]. The emission maxima of the cyanoam(m)ine complexes vary regularly between these extremes, changing from 680 nm in $Cr(NH_3)_5(CN)^{2+}$ to 777 nm in $Cr(NH_3)(CN)_5^{2-}$, i.e. the more numerous the CN^- ligands, the larger the displacement to the red.

Smaller shifts in the same direction are induced by decreasing the number of N–H bonds in the am(m)ine ligands, as observed in other $CrN_4X_2^+$ systems [15]. The *trans*- and *cis*-dicyano complexes of Table 6 present the energy sequence: $NH_3 > en \sim tn > macrocycle > bpy$, which also reflects the π-acceptor character of bpy. The peak positions and profiles are negligibly affected by amine deuteration [68,83].

The higher $^2T_1$ state is more susceptible to symmetry lowering: in some *trans*-CrN_4XY^+ species with large tetragonal distortions, its ^2E component may drop in energy and become the lowest doublet. Emission is then broad, due to a non-uniform occupation of the t_2 orbitals for this component, and is solvent- and temperature-dependent [15]. This is not the case with *trans*-$CrN_4(CN)_2^+$, at least when $N_4 = (NH_3)_4$ [23,78] and $(en)_2$ [34], as the bandshapes of these ions are very similar to those of the cis isomers and are fairly insensitive to the medium.

For solid and dissolved *trans*-Cr(cyclam)$(CN)_2^+$, four emission bands have been reported at 435, 523, 720 and 835 nm, and have been assigned to both fluorescence from $^4T_2$ and phosphorescence from various doublet states [80]. However, caution has been suggested in accepting this result, in view of the possibility of impurity emission, specially in the solid state [15].

For cationic cyanoam(m)ines, solvent effects on emission are generally slight, as those on absorption. The relatively large band shift of *trans*-$Cr(NH_3)_4F(CN)^+$ in water has been attributed to F–H interactions that would modify the nature of the F^- ligand [38].

Like $Cr(CN)_6^{3-}$ [79], the $Cr(NH_3)(CN)_5^{2-}$ anion emits in aprotic solvents but not in aqueous solution [45]. This failure is thought to have its origin in CN–H_2O hydrogen bonds providing good solute–solvent vibrational coupling enhancing ^2E radiationless deactivation.

Under a magnetic field, the intensity distributions of the phosphorescence spectra of *trans*-Cr(cyclam)$(CN)_2^+$ and *trans*-Cr([15]aneN_4)$(CN)_2^+$ are modified. This is explained by a Zeeman splitting of the low-lying doublet state(s) and consequent shifts in their population [81].

4.4 Charge-transfer transitions

The low-lying, unfilled π^* orbitals of cyanide are energetically suitable for the $t_2(Cr) \rightarrow \pi^*(CN)$ electron excitation. Such a fully allowed transition is indeed observed in $Cr(CN)_6^{3-}$ as a high-intensity band with maximum at 259 nm ($\varepsilon = 5940$). Theoretical background has been provided for its metal-to-ligand (MLCT) nature; the $\pi(CN) \rightarrow e^*(Cr)$ ligand-to-metal charge transfer (LMCT), possible in principle in all $M(CN)_6^{z-}$ complexes, is expected for Cr(III) at higher energies [84]. On the grounds of the close resemblance with $Cr(CN)_6^{3-}$, the UV spectral band of $Cr(NH_3)(CN)_5^{2-}$ is straightforwardly attributed to the same MLCT transition [45].

Several monocyano- [27,38] and dicyanoammine [23] ions exhibit characteristic short-wavelength absorption profiles with sequences of shoulders having fairly constant separations of ca. 1600 cm^{-1}. The data are assembled in Table 7. The MLCT (Cr-to-CN) assignment for such absorptions is supported by the regularity and the magnitude of the energy spacings, consistent with a vibrational progression of the C—N stretch in the excited state. The presence of a π^*(CN) electron is, in fact, expected to lower the stretching frequency with respect to the ground state (ca. 2100 cm^{-1}).

It should be noted that the MLCT transitions of cyanoam(m)ines are opposite in direction to the LMCT transitions of the majority of acidoam(m)ines, in parallel with the π-acceptor character of CN$^-$ and the π-donor character of the other simple acido groups.

TABLE 7

Cr-to-CN charge-transfer absorption features^a in aqueous solution

Complex	Wavelengths, nm^a (ε, M^{-1} cm^{-1})						Ref.
$Cr(NH_3)_5(CN)^{2+}$	251	241	232	224	217	210	27
	(60)	(200)	(440)	(760)	(1060)	(1330)	
trans-$Cr(NH_3)_4(CN)F^+$	246	236	227	220	213		38
	(45)	(160)	(300)	(450)	(640)		
trans-$Cr(NH_3)_4(H_2O)(CN)^{2+}$	251	241	232	224	217	211	38
	(75)	(230)	(480)	(750)	(1000)	(1300)	
trans-$Cr(NH_3)_4(CN)Cl^+$	250	239	231	223	216		38
	(140)	(700)	(2150)	(3800)	(6000)		
trans-$Cr(NH_3)_4(CN)_2^+$	250	240	231	224^b	216^b	209	23
	(155)	(610)	(1330)	(1610)	(1770)	(2530)	
cis-$Cr(NH_3)_4(CN)_2^+$	252	242	233	225	217		23
	(320)	(890)	(1230)	(1400)	(1650)		
$Cr(NH_3)(CN)_5^{2-}$	263	251^b	220				45
	(2450)	(3300)	(1950)				

^{a}Absorption shoulders, unless otherwise noted.

^{b}Absorption maximum.

In complexes containing both types of heteroligand, the two charge-transfers may occur at similar energies and the corresponding bands may overlap. The extinction coefficients of the *trans*-$Cr(NH_3)_4(CN)X^+$ ions with $X = F^-$ and Cl^- (and possibly $X = H_2O$) indicate that the underlying $\pi(X) \rightarrow e^*(Cr)$ transition predictably shifts to longer wavelengths as the optical electronegativity of X decreases. For $X = NCS^-$, the multiple LMCT band of thiocyanate (not included in Table 7) completely hides the MLCT band [38]. In the absence of other acido ligands, the intensities of the MLCT features increase with the number of cyanides, according to expectation.

The strong absorption of $(CN)(tmpa)Cr(\mu\text{-}O)Cr(tmpa)(CN)^{2+}$ near 350 nm (ε = ca. 12000) has been assigned as MLCT from Cr to bridging O on a MO basis; solvent effects supported the assignment [37].

Some cyano-bridged Cr(III)–M(II) dinuclear species present an intense UV band not seen in the separated mononuclear components. This is associated with a metal-to-metal charge transfer (MMCT) transition from the reducing M(II) to the oxidizing Cr(III) centre, mediated by the bridging ligand. For $(NH_3)_5Cr(\mu\text{-}NC)Fe(CN)_5^-$, the band is centred at 376 nm ($\varepsilon = 2400$) [57]. Analogous maxima of the $(H_2O)(en)_2Cr(\mu\text{-}NC)M(CN)_5^-$ complexes with M = Fe, Ru, and Os occur at 394 ($\varepsilon = 1880$), 298 ($\varepsilon = 2700$) and 318 nm ($\varepsilon = 2870$), respectively [62]. Absorptions of this kind have been observed in other heterometallic M(III)–M(II) systems [85].

Finally, in Cr–NC–Pt compounds [48,52,58,61], the new band at 305–310 nm is ascribed to Pt–Pt interactions related to bimolecular association and involving the d_{z^2} and p_z orbitals of Pt(II). Such an effect, characteristic of $Pt(CN)_4^{2-}$, appears to be considerably enhanced by Pt binding to Cr(III) [52].

4.5 *Excited-state absorption*

The transient absorption spectrum of the long-lived lowest doublet state of *trans*-$Cr(cyclam)(CN)_2^+$ has been measured by flash photolysis. The maxima at ca. 350 ($\varepsilon \approx 140$) and 420 nm ($\varepsilon \approx 70$) have been assigned to LF spin-allowed transitions to families of upper doublet levels derived from both the t_2^3 and t_2^2e electron configurations [81].

In the trinuclear species $[(NC)(cyclam)Cr(\mu\text{-}CN)]_2Ru(bpy)_2^{4+}$, the above-mentioned bands disappear while absorption by the Cr-localized doublet shows a new maximum at ca. 900 nm ($\varepsilon \approx 1500$), accompanied by a comparable bleaching at ca. 410 nm. The former has been attributed to a MMCT transition from Ru(II) to doublet-state *Cr(III), and the latter to depletion of the expected Ru(II) → ground-state Cr(III) MMCT transition that in this system is hardly detectable by ground-state spectroscopy. The spectral displacement between bleaching and absorption in fact matches the doublet-state energy [66].

5. GROUND-STATE SOLUTION CHEMISTRY

5.1 Aquation reactions

Two traits characterize the solution behaviour of Cr(III) cyanoam(m)ines: the high inertness in aprotic solvents and in neutral or alkaline aqueous media and, by contrast, the remarkable lability of CN^- in acidic solutions. Both are related to the large basicity of cyanide that, on one hand, lends strength to the Cr—CN bond, on the other hand, favours protonation of the coordinated ligand.

The acid-catalyzed aquation of cyanide has been investigated in the *trans*-$Cr(NH_3)_4X(CN)^{z+}$ series, where $X = NH_3$ [27], CN^-, H_2O [86], NCS^-, F^- and Cl^- [87]. In all cases, the pseudo-first-order rate constants, k_{obsd}, have been found to fit the general expression

$$k_{obsd} = \frac{k_0 + k_H K[H^+]}{1 + K[H^+]} \tag{1}$$

which describes CN^- loss in terms of two competing routes: an acid-independent (k_0) and an acid-dependent pathway (k_H), consequent to instantaneous and reversible protonation of the reactant, according to the scheme

$$\begin{tikzcd}
CrN_4X(CN)^{z+} + 2H_2O \arrow[r, "k_0"] \arrow[d, shift right, swap, "K"] & CrN_4X(H_2O)^{(z+1)+} + HCN + OH^- \\
CrN_4X(CNH)^{(z+1)+} + H_2O \arrow[r, "k"] \arrow[u, shift right, swap, "H^+"] & CrN_4X(H_2O)^{(z+1)+} + HCN
\end{tikzcd} \tag{2}$$

Table 8 reports the rate and equilibrium constants of eqn. (1), as well as the activation parameters for the acid-assisted processes. The table includes partial data for cis complexes [23,73] and, for comparison, those relative to some cyanoaquo compounds [88,89].

5.1.1 Acid-independent aquation

k_0 is always various orders of magnitude smaller than k_H, indicating that the contribution of the unprotonated forms to reactivity is generally unimportant under ordinary conditions. In some instances, only upper limits could be set for k_0. This is a result of the strong σ bonding of CN^-, synergetically stabilized by π back-donation. In fact, in the $Cr(NH_3)_5X^{2+}$ or $Cr(H_2O)_5X^{2+}$ series, correlations with either σ and π effects (as expressed by the AOM parameters), or the base strengths of X^-, place CN^- at the lower end of a scale of leaving capability for the common monodentate acido groups [27].

TABLE 8

Rate and equilibrium constants at 25°C and activation parameters for cyanide aquation of Cr(III) cyanoam(m)ine and cyanoaquo complexes[a]

Complex	$10^5 k_O$ (s^{-1})	$10^3 k_H K$ ($M^{-1} s^{-1}$)	$10^3 k_H$ (s^{-1})	K (M^{-1})	$\Delta H^{\neq b}$ (kJ mol^{-1})	$\Delta S^{\neq b}$ (J K^{-1} mol^{-1})	Ref.
$Cr(NH_3)_5(CN)^{2+}$	<0.01	4.10	14.7	0.28	72	−39	27
trans-$Cr(NH_3)_4(CN)_2^+$	<2	450	107	4.2	70	−29	86
trans-$Cr(NH_3)_4(H_2O)(CN)^{2+}$	0.48	0.35	13	0.028	71	−42	86
trans-$Cr(NH_3)_4(CN)F^+$	4.8	29.6	14	2.1	86	−4	87
trans-$Cr(NH_3)_4(CN)Cl^+$	<1	4.1	7	0.6	86	−22	87
trans-$Cr(NH_3)_4(CN)(NCS)^+$	0.9	2.7	7	0.4	78	−32	87
cis-$Cr(NH_3)_4(CN)_2^+$		~5[c]					23
cis-$Cr(NH_3)_4(H_2O)(CN)^{2+}$		~5[c]					23
cis-$Cr(en)_2(CN)_2^{+}$[d]	0	19.9			78	−16	73
$Cr(H_2O)_5(CN)^{2+}$	1.1	0.590	3.2	0.19	68	−67	88
cis-$Cr(H_2O)_4(CN)_2^+$	<0.6	0.84	1.5	0.55	67	−75	89
fac-$Cr(H_2O)_3(CN)_3$	<0.3	0.66	0.58	1.1	67	−79	89

[a] Ionic strength $\mu = 2.0$ M ($NaClO_4$), unless otherwise noted.

[b] Activation parameters for k_H; when $k_H K$ is not separable, the parameters refer to the product of the two constants.

[c] Semiquantitative estimate.

[d] $\mu = 1.0$ M (NaCl).

5.1.2 *Acid-assisted aquation and kinetic trans effects*

The lability of cyanide is greatly enhanced by protonation, as expected from a decreased nucleophilicity and an increased ligand repulsion consequent to removal of the negative charge. Consistently, the activation enthalpies for the k_H paths are somewhat smaller than usual in Cr(III) aquation [1,6–9].

Along a given series of compounds, k_H normally increases with the complex charge, the variation being not as marked as that found when the leaving groups are negative [1,6]. In the trans series, the exceptionally high k_H value of *trans*-$Cr(NH_3)_4(CN)_2^+$ attests to the large trans-labilizing effect of CN^-. Such an effect is even more apparent if comparison is made with the much lower reactivities of the cis-dicyano and fac-tricyano complexes, where the cyanides are opposite to either N- or O-coordinated ligands.

Also, the k_H value of *trans*-$Cr(NH_3)_4(CN)F^+$, apparently anomalous for a monopositive species, denotes some kinetic trans influence of F^-, whose σ-donor (AOM) ability is proximate to that of CN^- [13]. This is congruent with the relevant role of σ-donation in trans effects of octahedral complexes [90,91], as opposed to that of π-acceptance in square planar systems.

The X ligand of *trans*-$Cr(NH_3)_4(CN)X^+$ may be released in parallel with CN^-. This is the case with $X = Cl^-$, again ascribed to trans activation by CN^-. Loss of chloride is pH-independent, and the rates for the two modes become comparable around pH 1. No such process is observed instead when $X = F^-$ or NCS^-, in agreement with the stronger Cr–X bonds in these systems [87].

5.1.3 *Protonation of coordinated cyanide and thermodynamic trans effects*

The equilibrium constants for proton uptake predictably tend to be larger the smaller the cationic charge. The steady variation of K for the three differently charged cyanoaquo complexes, all having H_2O trans to CN^-, indicates that the only significant effect is here the electrostatic one.

The less uniform behaviour of the trans tetraammines, where the acid strengths of the $Cr(NH_3)_4X(CNH)^{z+}$ ions increase in the order

$$X = CN^- < F^- < Cl^- < NCS^- < NH_3 < H_2O \qquad (3)$$

suggests other factors to be operative in this series. One factor must be the electronegativity of X that, with the exception of $X = F^-$, parallels the sequence of acidity of eqn. (3). In addition, both the latter exception and the comparatively large value of K for $X = CN^-$ reveal thermodynamic trans effects, also ascribable to the high donor power of fluoride and cyanide [87].

In summary, the overall chemical change, substantially described by the $k_H K$ product (not separable into the individual constants when $K[H^+] \ll 1$ [73]), exhibits different patterns in the two groups. While in the three cyanoaquo species the regularly opposing trends of k_H and K determine similar aquation rates, in the cyanoammines, various trans effects differentiate the reactivities over a thousandfold range. It is notable that *trans*-dicyano complexes aquate faster than their cis isomers, in contrast to the usual behaviour of the *trans*/*cis*-diacidotetraam(m)ine pairs [1,6].

5.1.4 Stereochemistry

All the *trans*- and *cis*-tetraam(m)ines of Table 8, as well as the *trans*-$CrN_4(CN)_2^+$ ions where N_4 = cyclam [28], tet*a* [29] and tn [31], were found to aquate with complete retention of configuration. Interestingly, both substitution steps of $(-)_D$-*cis*-$Cr(en)_2(CN)_2^+$ were also demonstrated to proceed with full retention of optical activity [73].

The isomeric purity of the acidoaquo and/or diaquo products provided the main piece of evidence for the geometries of these complexes. Stereoretentivity is typical of ground-state substitution reactions of Cr(III) in aqueous solution. It is regarded as an attribute of the associative interchange (I_a) mechanism, in contrast with the steric change usually characterizing dissociative-type (I_d or D) mechanisms of other octahedral systems [7,24]. Although not diagnostic, the negative entropies of activation are compatible with an associative model for CN^- aquation in Cr(III).

5.1.5 An edta system

A kinetic study of $Cr(Y)(H_2O)(CN)_2^{3-}$ in the pH range 2–7 [25], showed the occurrence of slow-fast two-step CN^- aquation. The apparent first-order rate constants varied with the acidity according to a titration-like curve, fitting the equation

$$k_{obsd} = \frac{k_1[H^+]}{K + [H^+]} \tag{4}$$

and consistent with the sequence

$$\begin{tikzcd}
Cr(YH_x)(H_2O)(CN)_2^{2-} \arrow[r, shift left, "K"] \arrow[d, "k_1"', "-CN^-"] & Cr(YH_{x-1})(H_2O)(CN)_2^{3-} + H^+ \arrow[l, shift left] & \\
Cr(YH_x)(H_2O)(CN)^- \arrow[r, "k_2", "-CN^-"'] & Cr(YH_x)(H_2O) & k_2 \gg k_1
\end{tikzcd} \tag{5}$$

where $k_1(25°C) = 4.6 \times 10^{-2}\ s^{-1}$, $\Delta H^{\neq} = 79\ kJ\ mol^{-1}$, $\Delta S^{\neq} = -6\ J\ K^{-1}\ mol^{-1}$, and $K(25°C) = 3.7 \times 10^{-6}$ M. The index x for protonation of Y ($1 \leqslant x \leqslant 3$) could not be established, although K was ascertained to describe a single stage of acid-base equilibrium. Furthermore, the K value was judged to be too small for such an equilibrium to involve coordinated CN^- (cf. Table 8). The possibility was considered that the comparatively fast aquation of CN^- be due to an internal acid catalysis via hydrogen-bond formation between a cyano ligand and the protonated free carboxyl group of the edta ligand.

5.2 Linkage isomerization

In the presence of Ag^+, aqueous *cis*-$Cr(en)_2(CN)_2^+$ undergoes a fast reaction, strongly competitive with Ag^+-catalyzed release of CN^-. The product of such non-aquation reaction was inferred to be *cis*-$Cr(en)_2(NC)_2^+$ on the basis of its UV-Vis spectrum (maxima at 458 and 351 nm) matching the LF features of a CrN_6 chromophore, and of its CD spectrum indicative of stereoretention [73].

Cyano-isocyano isomerism, induced by Ag^+ or Hg^{2+} in several Cr(III)-cyanoaquo complexes, may be schematized as

$$\text{Cr—CN} + Ag^+ = \text{Cr—NCAg}^+ \qquad (6)$$

where cation association stabilizes the isocyano coordination. An important role is thought to be played by the affinity of the softer-base C end of cyanide for the soft acids Ag^+ and Hg^{2+} [92,93].

A 1:1 adduct was isolated as a salt of empirical formula $[Cr(en)_2(NC)_2Ag](ClO_4)_2$, in which Ag^+ was proposed to interact with both NC^- groups retaining their cis arrangement. Significantly, Ag^+ removal by I^- precipitation regenerated the Cr—CN bonds [73].

Cr—NC bonding was subsequently proven by X-ray structural determination of the 1:2 silver adduct of the same dicyano complex, *cis*-$Cr(en)_2(NCAgCN)_2^+$ (Sect. 3.1), where the $Ag(CN)_2^-$ groups were found to act as N-coordinating ligands [70].

The association constants of *cis*-$Cr(en)_2(CN)_2^+$ with various cations in aqueous solution were estimated to be $>10^5$, 3.6×10^2 and $35\ M^{-1}$ for Ag^+ [73], Cu^{2+} and Cd^{2+} [70], respectively, in fair correlation with the softness of the metal ions.

Also, high acid concentrations appear to induce linkage isomerization. For various members of the *trans*-$Cr(NH_3)_4X(CN)^{z+}$ series, spectral and kinetic evidence has recently been obtained [87] that at $[H_3O^+] > 0.3$–0.6 M rapid (but not instantaneous) and reversible Cr—CN/Cr—NC interconversion is superimposed to the early stages of acid-catalyzed aquation. The inverse dependence on $[H_3O^+]$ for the rate of the fast process and the associated red shifts of the LF bands suggest a reaction sequence of the type

$$\begin{tikzcd}
\text{Cr—CN} + H^+ \arrow[r, shift left, "K_1"] \arrow[d, shift right, "k_2"'] & \text{Cr—CNH} \arrow[l, shift left] \arrow[r, "k_1"] & \text{Cr—OH}_2 + \text{HCN} \\
\text{Cr—NC} + H^+ \arrow[u, shift right, "k_3"'] \arrow[r, shift left, "K_2"] & \text{Cr—NCH} \arrow[l, shift left] & k_3 > k_2 > k_1
\end{tikzcd} \qquad (7)$$

in which a mixture of the two isomers is rapidly attained (k_2) upon acidification of the cyano complex: the higher the acidity, the larger the fraction of Cr—NC isomer. The latter would gain stability through protonation, since NCH is presumed to be a weaker acid than CNH ($K_2 > K_1$). Such a mixture, in virtual equilibrium (k_2/k_3), is then expected to disappear mainly, if not solely, through aquation of the more labile Cr—CNH species with a k_1 rate-determining step. This picture finds support in previous kinetic indications that, in a similar pH range, the isocyano ligand of $Cr(H_2O)_5(NC)^{2+}$ is involved both in a protonation equilibrium and in fast reversion to the cyano configuration [94].

5.3 Acid–base properties

As mentioned in Sect. 2.5, the hydroxo counterparts of some cyanoaquo complexes proved sufficiently stable to be isolated and to allow determination of the H_2O dissociation constants. For *trans*- and *cis*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$, the concentration pK_a values were found to be 5.5 and 5.6, respectively. The lack of the usual discrimination between *trans*- and *cis*-acidoaquoam(m)ines and the closeness to the acidity of $Cr(NH_3)_5(H_2O)^{3+}$ were attributed to balancing of the strong σ-donor and fair π-acceptor properties of CN^-, resulting in an inductive effect comparable with that of NH_3, weaker σ-donor only [23].

Along the series $X(tmpa)Cr(\mu\text{-}OH)Cr(tmpa)X^{3+}$, where $X = N_3^-, NCO^-, NCS^-$ and CN^-, the last is the strongest acid, with $pK_a = 0.64$. The acid strength has been related to d(Cr)–p(O) π interactions: the stronger such bonding in the linear Cr—O—Cr deprotonated form, the higher its resistance to protonation to give the presumably bent Cr—(OH)—Cr form [37].

6. PHOTOCHEMISTRY

The excited-state chemistry of Cr(III) complexes has been extensively explored and thoroughly studied, under an intense mutual stimulation of experiment and theory [9–14]. LF states have received major attention, with particular regard to: (1) the selectivity of ligand labilization, (2) the stereochemistry of photosubstitution, and (3) the chemical role of the two lowest excited states of different spin multiplicity.

The cyanoam(m)ines have provided important test cases in the course of this growth, thanks to the following peculiarities. (1) The uncommon ordering of the LF energy levels, which enables full access to states that in other acidoam(m)ines can only be populated indirectly and to limited extents, at the most. (2) The fairly intense and long-lived emission under photolysis conditions. (3) The relatively wide gap between the photochemically relevant, lowest quartet and doublet excited states, that increases with the number of CN^- groups: the energy of the spin-allowed transitions is, in fact, progressively raised by the intensified field strength, while that of the spin-forbidden ones is simultaneously depressed by the nephelauxetic effect.

6.1 Preferential ligand photosolvation

All Cr(III) photolysis models have been related to the properties of the lowest quartet excited state(s). Successive elaborations of the early idea of photolabilized axis [95] have led to the recognition of σ and π contributions to the weakening of the various Cr—L bonds [96,97] and, finally, to a quantification of their excited-state strengths as a function of the σ_L and π_L spectrochemical parameters in the framework of AOM theory [13]. Such developments have been reviewed several times [10–14]. Table 9 gathers the quantum yields for ligand substitution of cyanoam(m)ine complexes, and Table 10 compares the findings with the theoretical expectations, listed chronologically as follows.

(A) Adamson's rules, predicting substitution of the strong-field ligand on the weak-field axis [95].

(B) Zink's and Wrighton's approaches based on σ-bond labilization along such an axis, coupled with further destabilization of π-acceptors such as CN^-, and stabilization of π-donors like other acido groups [96,97].

(C) Vanquickenborne–Ceulemans' AOM estimates of bond energies in the lowest excited quartet state [13].

The most detailed investigations have, naturally, dealt with trans systems where axial/equatorial distinction is clear-cut. As mentioned in Sect. 4.1, in the *trans*-$CrN_4X_2^+$ series the low-energy component of the split $^4T_2$ state is ^4E for $X \neq CN^-$ and $^4B_2$ for $X = CN^-$, respectively associated with axial (prevalently d_{z^2}) and equatorial ($d_{x^2-y^2}$) antibonding electron densities.

In agreement with all the theories, the dominant, or unique LF reaction mode of *trans*-$CrN_4(CN)_2^+$ ions is release of equatorial am(m)ine, as opposed to preferred loss of axial X in other *trans*-diacido compounds. (Excluded from this comparison is the $X = F^-$ species, where Cr—N bond rupture is a consequence of the large Cr—F bond strength even in the ^4E state [13,16,98]. For $N_4 = (NH_3)_4$ [43] and $(en)_2$ [22], am(m)ine aquation is indeed the sole photoprocess.

TABLE 9

Quantum yields for ligand photosolvation

Complex	Medium[a]		λ_{irr} (nm)	Band[b]	Φ_N[c]	Φ_{CN^-}	Φ_X	Ref.
	pH	(μ, M)						
$Cr(NH_3)_5(CN)^{2+}$	3.0	(0.50)	495	LF1	0.33	<0.0005		99
			455	LF1	0.33	<0.0005		99
			420	LF1	0.33	<0.0005		99
			350	LF2	0.33	<0.0005		99
			250	CT	0.31	<0.0005		99
			235	CT	0.34	<0.0005		99
trans-$Cr(NH_3)_4(CN)_2^+$	3.8	(0.04)	480	LF1	0.24	<0.005		43
			440	LF1	0.24	<0.005		43
			410	LF1	0.24	<0.005		43
			350	LF2	0.24	<0.005		43
trans-$Cr(en)_2(CN)_2^+$	2.7		436	LF1	0.6	<0.02		22
			366	LF2		<0.05		22

TABLE 9 (*continued*)

Complex	Medium[a]		λ_{irr} (nm)	Band[b]	Φ_N[c]	Φ_{CN^-}	Φ_X	Ref.
	pH	(μ, M)						
trans-$Cr(tn)_2(CN)_2^+$	3	(0.1–0.05)[d]	458	LF1	0.05	0.02		31
			436	LF1	0.05	0.03		31
trans-$Cr(cyclam)(CN)_2^+$	3.0[e]		436	LF1	$<10^{-5}$	$<10^{-5}$		83
trans-Cr(tet*a*)$(CN)_2^+$	[e]		436	LF1	$<10^{-5}$[f]	$<10^{-5}$[f]		29
trans-$Cr(NH_3)_4(H_2O)(CN)^{2+}$	3.0	(0.10)	465	LF1	0.06	0.06	0.12[g]	77
			355	LF2	0.06	0.07	0.10[g]	77
trans-$Cr(NH_3)_4(NCS)(CN)^+$	3.0	(0.10)	505	LF1	0.25	0.06	0.020	77
			465	LF1	0.25	0.08	0.018	77
			360	LF2	0.25	0.06	0.020	77
			295	CT	0.20	0.06	0.06	102
			250	CT	0.21	0.06	0.10	102
trans-$Cr(NH_3)_4F(CN)^+$	3.0	(0.10)	485	LF1	0.32	0.10	0.011	77
			360	LF2	0.33	0.07	0.009	77
trans-$Cr(NH_3)_4Cl(CN)^+$	3.0		540	LF1	0.08	0.32	<0.02	82
			490	LF1	0.09	0.31	<0.02	82
			365	LF2	0.09	0.31	<0.02	82
			245	CT	0.16	0.14	0.06	82
cis-$Cr(NH_3)_4(CN)_2^+$	3.3	(0.10)	480	LF1	0.25	0.010		44
			435	LF1	0.26	0.022		44
			405	LF1	0.30	0.020		44
			350	LF2	0.24	0.015		44
cis-$Cr(en)_2(CN)_2^+$	2.7		436	LF1	0.51	0.09		22
			366	LF2	0.45	0.10		22
$Cr(edta)(H_2O)(CN)_2^{3-}$	7.14[h]		514	LF1		0.016		25
	7.66[h]		514	LF1		0.018		25
	8.04[h]		514	LF1		0.019		25
	8.58[h]		514	LF1		0.021		25
	9.13[h]		514	LF1		0.023		25
$Cr(NH_3)(CN)_5^{2-}$	3.3		400	LF1	0.08	0.06		45
	7.2[i]		400	LF1	0.08	0.06		45
	dmso		400	LF1	0.05	0.007		45
	dmf		400	LF1	0.11	0.003		45

[a] Aqueous $HClO_4$ solutions at the given pH and ionic strength ($NaClO_4$, in parentheses) unless otherwise noted; room-temperature.

[b] LF1 and LF2 denote the $^4A_2 \rightarrow {}^4T_2$ and $^4A_2 \rightarrow {}^4T_1$ excitations, respectively, in O_h approximation.

[c] Quantum yields for am(m)ine labilization.

[d] $KClO_4$.

[e] HNO_3 solution.

[f] Reported photoinertness; upper limits are set by analogy with the cyclam complex.

[g] Quantum yield for trans → cis isomerization, taken to measure H_2O photoexchange.

[h] ca. 0.5 M tris(hydroxymethyl)aminomethane buffer.

[i] Phosphate buffer.

TABLE 10

Predicted and observed ligand-field photosolvation modes

Complex	Photoactive state	Labilized bonds		(C)[c]			Observed modes[d]
		(A)[a]	(B)[b]	I*(Cr-L), μm^{-1}			
				N_{eq}	CN^-	N_{ax}	
$Cr(NH_3)_5(CN)^{2+}$	$^4B_2$	N	N_{eq}	0.90	1.75	1.44	NH_3
				N	CN^-	X	
trans-$Cr(NH_3)_4(CN)_2^+$	$^4B_2$	N	N	0.90	1.75		NH_3
trans-$Cr(en)_2(CN)_2^+$	$^4B_2$	N	N	0.91	1.75		en
trans-$Cr(tn)_2(CN)_2^+$	$^4B_2$	N	N	0.90	1.75		$tn > CN^-$
trans-$Cr(NH_3)_4(H_2O)(CN)^{2+}$	^4E[e]	[f]	$(CN^- > X)$[g]	1.17	1.09	0.90	$X > CN^- \sim NH_3$
trans-$Cr(NH_3)_4(NCS)(CN)^+$	$^4B_2$[e]	[f]	$(CN^- > X)$[g]	0.90	1.76	1.36	$NH_3 > CN^- > X$
trans-$Cr(NH_3)_4F(CN)^+$	^4E[e]	[f]	$(CN^- > X)$[g]	1.14	1.16	1.53	$NH_3 > CN^- > X$
trans-$Cr(NH_3)_4Cl(CN)^+$	^4E	CN^-	$CN^- > X$	1.17	1.08	0.96	$CN^- > NH_3$
				N_{eq}	CN^-	N_{ax}[h]	
cis-$Cr(NH_3)_4(CN)_2^+$	^4E	N	N_{ax}[h]	1.19	1.45	0.86	$NH_3 > CN^-$
cis-$Cr(en)_2(CN)_2^+$	^4E	N	N_{ax}[h]	1.20	1.44	0.87	$en > CN^-$
				CN_{eq}	CN_{ax}	N	
$Cr(NH_3)(CN)_5^{2-}$	^4E	CN^-	CN_{ax}	1.45	1.03	0.85	$NH_3 > CN^-$

[a] Adamson's rules [95].

[b] σ/π MO qualitative models [96,97].

[c] Excited-state bond energies calculated according to the AOM model [13].

[d] See Table 9.

[e] Formally lowest excited quartet state: ^4E and $^4B_2$ are almost degenerate.

[f] Uncertain prediction, as the three axes have similar average ligand-field strengths.

[g] Prediction limited to competitive axial labilization.

[h] N–Cr–N designated as the z axis.

When N_4 = cyclam [83] and teta [29], N detachment is precluded by the macrocyclic amines while CN^- remains firmly bound, so that, remarkably, these complexes are completely photoinert.

In the case of $N_4 = (tn)_2$, definite CN^- solvation has been observed in addition to amine solvation, and has been justified by steric effects of the six-membered chelate ring, which would make tn a reluctant leaving ligand, while promoting axial bond cleavage [31].

Also, $Cr(NH_3)_5(CN)^{2+}$ undergoes exclusive NH_3 aquation [99]. The general problem with the pentaammines, however, is that the original axial or equatorial site of displaced ammonia cannot be identified, owing to the steric changes that accompany Cr(III) photolysis. Despite this uncertainty, the isomeric distribution of the products (vide infra), which is different from that of other $Cr(NH_3)_5X^{2+}$ systems (again excepting $X = F^-$) but parallels that of *trans*-$Cr(NH_3)_4(CN)_2^+$, is congruent with photoaquation of in-plane NH_3.

The constancy of quantum yields throughout the LF region denotes a negligible involvement of the ^4E state, that in *trans*-dicyano complexes lies ca. 2500 cm^{-1} (or 12 RT) above $^4B_2$.

In *cis*-$CrN_4(CN)_2^+$, the state order is reversed. Of the two sublevels of $^4T_2$ (in D_{4h} approximation), ^4E is the lower in energy, with its antibonding charge localized mainly on the unique N—Cr—N axis. The major photoaquation path for both the NH_3 [44] and en [22] complexes involves Cr—N bond rupture, as anticipated by all models. In addition to this path, there are appreciable yields of CN^-.

On the basis of the excited-state bond energies, CN^- is unlikely to arise from ^4E. This circumstance and the dependence of both quantum yields (and of the product isomer distribution, see next section) on the excitation energy, demand the participation of the upper $^4B_2$ state, more inclined than ^4E to Cr—N bond fission. A gap of ca. 1250 cm^{-1} would allow some thermal equilibrium between the two levels. Another suggested possibility, consistent with the wavelength dependence, is branching to $^4B_2$ and ^4E in various proportions during relaxation of Franck–Condon states [11]. Such an occurrence would also accommodate the variation of Φ_{CN^-} for *trans*-$Cr(tn)_2(CN)_2^+$ [31]. It should be noted that in *cis*-$CrN_4X_2^+$, although the photoactive states are different for $X \neq CN^-$ and $X = CN^-$, there is no difference in the type of ligand preferentially lost; that is, in both cases prevalent am(m)ine aquation, whether "axial" or "equatorial", is expected [13] and found [22,44]. Furthermore, as for the pentaammines, information is missing on the initial position of the photolabilized Cr—N bond.

The *trans*-$Cr(NH_3)_4X(CN)^{z+}$ ions with $X = H_2O$, NCS^- and F^- are specially interesting since CN^- and X act oppositely on the splittings of the O_h states, so that separations of only 100–300 cm^{-1} make ^4E and $^4B_2$ nearly degenerate. As a result, CN^-, X and NH_3 are photoaquated to comparable extents and, in the absence of any significant axial/equatorial differentiation, the σ and π bonding properties of the three ligands remain the relevant factors [77]. These species are, therefore, highly diagnostic toward the photolysis models, in particular toward the AOM model [13].

Table 10 shows the general correctness of this theory in predicting not only which group is preferentially lost but, for $X = H_2O$ and F^-, also the order of leaving ability of the other ligands. The discrepancy for $X = NCS^-$ (predicted, $\Phi_{CN^-} < \Phi_{NCS^-}$; found, $\Phi_{CN^-} > \Phi_{NCS^-}$) has been ascribed to imprecision of the available σ_{NCS^-} and π_{NCS^-} parameters [77], but may be also related to a trans effect, such as that exhibited by the analogous complex with $X = Cl^-$ [82]. The quantum yields for the three modes, essentially wavelength-independent, are consistent with all photoreactions originating from the same $^4B_2/^4E$ Boltzmann proportion.

Trans-$Cr(NH_3)_4Cl(CN)^+$ also has a pair of weak-field/strong-field ligands, but the very low spectrochemical position of Cl^- now brings ^4E ca. 800 cm^{-1} below $^4B_2$. Accordingly, 4/5 of the photochemistry is axial, with large yields of CN^- and undetectable loss of Cl^- [82]. The observed reactivity ($\Phi_{CN^-} \gg \Phi_{Cl^-}$) is in sharp contrast with that ($\Phi_{CN^-} < \Phi_{Cl^-}$) semiquantitatively predicted by model (C), although there is a fortuitous agreement with the qualitative expectations of (A) and (B). Together with σ-bond weakening, population of d_{z^2} is indeed expected to weaken the Cr—CN π bond and to strengthen the Cr—Cl bond; however, model (C) evaluates these changes as insufficient to favour CN^- labilization because the strong ground-state σ bonding of cyanide retains importance both in ^4E and (to a larger extent) in $^4B_2$.

The proposed explanation for such a notable disagreement is a kind of excited-state trans effect. It has been pointed out that excited-state bonding changes should not be regarded as independent of each other: mutual interaction of the good π-donor and π-acceptor abilities of Cl^- and CN^- may give rise to a push–pull action through the emptied d_{xz}/d_{yz} orbitals of Cr, providing extra stabilization for Cl^- and destabilization for CN^- [82]. Interestingly, this effect is opposite to the ground-state trans effect, whereby CN^- enhances the solvation of Cl^- [38].

LF photolysis of $Cr(NH_3)(CN)_5^{2-}$ in various solvents results in the displacement of NH_3 accompanied by lesser amounts of CN^-, which theory suggests to be axial [45]. This complex again discriminates between the AOM and the earlier models: the latter would incorrectly anticipate preference for CN^- loss by disregarding the initial large strength of the Cr—CN bonds.

The pentacyano system features a considerable solvent dependence. On passing from water to aprotic media, Φ_{NH_3} is little affected, while Φ_{CN^-} decreases by one order of magnitude. The 30-fold variation of the Φ_{NH_3}/Φ_{CN^-} ratio has been ascribed to the capability of coordinated cyanide to hydrogen-bond with the facing H atoms of water. This interaction would assist solvent interchange with CN^- in H_2O, but not in dmso and dmf. Mixed-ligand anionic complexes would thus be more suited than cationic ones to bring out medium effects on the release of negative ligands, because of the appropriate solvent orientation [45]. These observations emphasize the importance of chemical factors, in addition to the electronic factors, in determining the photolysis patterns, and support the associative nature of Cr(III) photosubstitution: photolabilization is far from being a merely intramolecular process.

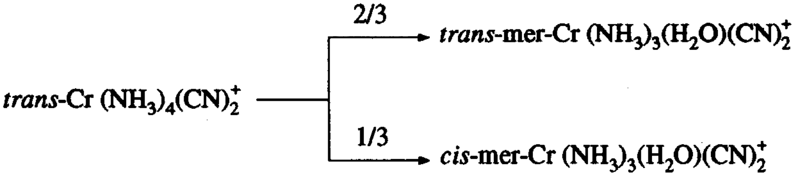
6.2 *Photostereochemistry*

Geometrical change is typical of Cr(III) photoaquation [10–14], in contrast to the stereoretentivity of thermal aquation [7,24].

Axial ligand photolysis is a common mode, for which complete trans → cis rearrangement seems not only customary, but also necessary [10,11]. Not surprisingly, the products of axial bond cleavage of *trans*-$Cr(NH_3)_4Cl(CN)^+$ [82] and *trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$ [77] are cis. The quantum yield for photoisomerization of the latter can thus be taken as a measure of H_2O exchange.

Trans-$Cr(NH_3)_4(CN)_2^+$ and, most likely $Cr(NH_3)_5(CN)^{2+}$, are among the few complexes subject to equatorial photosolvation. For CrN_4X_2 systems, there are three possible CrN_3SX_2 products (S = solvent).

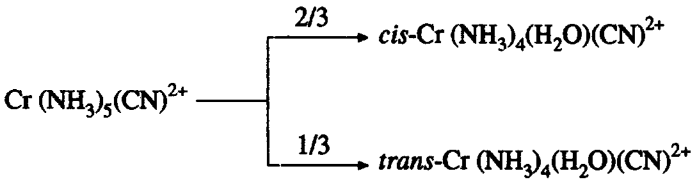
Photoaquation of the *trans*-dicyano complex is stereoselective, in that it leads to only two of the three dicyanoaquo species, both meridional, with trans-mer/cis-mer proportion of ca. 2:1 [43].



(8)

While the cis-mer product implies steric change, the trans-mer may arise by a retentive or non-retentive pathway: systems of this type are, therefore, inherently limited in establishing whether stereorearrangement is truly complete.

The monocyano complex photolyzes to give a mixture of *cis*- and *trans*-cyanoaquo isomers, again in a 2:1 ratio [99].

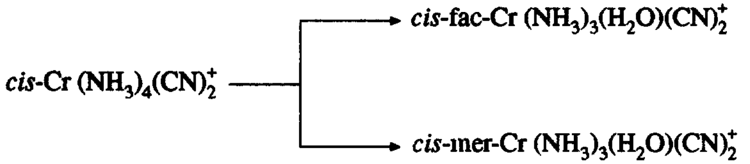


(9)

Even though, in this case, the stereochemistry is further entangled by the possibility of axial NH_3 release, some light is cast by analogy with *trans*-$Cr(NH_3)_4(CN)_2^+$. High, if not exclusive, preference for equatorial labilization is suggested by the same photoactive (in-plane antibonding) $^4B_2$ state and the same product distribution. As the pentaammine and the tetraammine differ by one axial ligand, the cis and trans-mer (with H_2O cis to both cyanides) species, as well as the trans and cis-mer (with H_2O trans to one CN^-) species, may be regarded as analogues. Whatever the mechanism, it should be the same for the two complexes. This interpretation is supported by the general finding that axial photolysis of $Cr(NH_3)_5X^{z+}$ and *trans*-$Cr(NH_3)_4XY^{z+}$ ions gives rise to only one isomer of cis geometry [10,11].

Trans-$Cr(tn)_2(CN)_2^+$ undergoes both axial and equatorial ligand loss: photolyzed solutions have been found to contain three photo products, the nature of which were inferred from chromatography and thermal reactivity [31]. The *cis*-$Cr(tn)_2(H_2O)(CN)^{2+}$ product is that expected from CN^- photoaquation. The others, related to tn aquation, are *trans*- and *cis*-$Cr(tn)(tnH)(H_2O)(CN)_2^{2+}$, their ratio being ca. 7 at 488 nm and ca. 5 at 458 nm. The steric relationship is known for the CN^- groups, but not for H_2O and the dangling tnH^+ chain.

Similarly to its trans counterpart, *cis*-$Cr(NH_3)_4(CN)_2^+$ stereospecifically yields two of the three possible products of NH_3 release. The pair is different and consists of *cis*-dicyano isomers: their proportion is ca. 2:1 or ca. 1:1, depending on whether the first or the second LF band is irradiated [44].



(10)

As stated earlier, *cis*-diacido complexes are per se not unambiguous, because NH_3 may have "axial" or "equatorial" origin. Moreover, in this case, nothing can be learned about possible stereomobility, since the cis position of the CN^- ligands is retained.

In spite of the above limitations, the complementary selectivity of *trans*- and *cis*-$Cr(NH_3)_4(CN)_2^+$ affords a diagnosis of the mechanistic models, the details of which have been surveyed elsewhere [11,13].

The associative-type model proposed by Kirk [11] postulates solvent entry trans to the leaving ligand, and the expectations are substantially those of the edge-displacement mechanism.

In both systems, the actual products are indeed those predicted by this model if, for the cis complex, NH_3 loss is restricted to the NH_3—NH_3 axis as theory suggests. Statistical solvent attack would result in 1:1 ratios of the following $Cr(NH_3)_3(H_2O)(CN)_2^+$ isomers (the octahedral edges approached by H_2O are in parentheses): *trans*-mer (N—N) and *cis*-mer (N—CN) for the *trans*-dicyano complex; *cis*-fac (N—CN) and *cis*-mer (N—N) for the *cis*-dicyano complex. The deviations from such ratios would be accommodated by preferential in-plane (N—N) association (favoured by the vacant d_{xy} orbital) plus mutual CN^- repulsion in the trans case [43], and preferential migration of the negative cyanides away from entering H_2O (N—CN) in the cis case [44].

The treatment developed by Vanquickenborne and Ceulemans in a dissociative context envisages a symmetry-restricted collapse of the square-pyramidal fragment to a trigonal bipyramid (tbp) in either its ground (g.s.) or excited state (e.s.), followed by orbital-oriented solvent attack in the trigonal plane [13].

This theory also accounts for the two observed isomeric couples. For *trans*-$Cr(NH_3)_4(CN)_2^+$ it requires both $^4B_2$ and ^4E reaction through the respective g.s. tbp intermediates having axial or equatorial CN^- pairs, and leading to trans-mer and cis-mer species. To explain the stereochemistry of the cis complex, only ^4E needs to be invoked, generating an e.s. tbp with one axial and one equatorial CN^-. Addition of H_2O would give the cis-fac isomer if it occurred in the e.s., and the cis-mer isomer if the tbp had meanwhile decayed to its g.s.

The picture, however, is not fully consistent with the wavelength profiles of the mode yields and isomer ratios, that would rather imply one state for the trans and two states for the cis system. The increased cis-mer percentage of the latter at higher energy may be justified by participation of $^4B_2$ (also reacting via a g.s. and an e.s. tbp), in line with the larger Φ_{CN^-} values; yet the trans-mer isomer expected from the e.s. tbp is absent. This example shows that in the cases where e.s./g.s. branching of the tbp is allowed for, the predictive ability of the model is lessened.

Though incomplete, the steric information on the products of tn detachment in *trans*-$Cr(tn)_2(CN)_2^+$ [31] is compatible with both approaches, particularly with the dissociative one, assuming $^4B_2/^4E$ reaction congruent with the wavelength dependence.

Obviously, axial photolysis is little diagnostic, as both models equally well rationalize the single cis product [11,13].

A final, general remark is that, while the dissociative model is quite satisfactory as to its predictions, it can hardly be reconciled with much of the chemical evidence, like anation behaviour, solvent effects and activation volumes, that argue in favour of associative or concerted pathways [11]. The reason for a dissociative choice was that an equivalent associative model failed to generate electronic selection rules in agreement with the observed stereomobility [13].

6.3 The reactive state(s)

Clues as to the excited states from which chemistry actually proceeds have frequently been sought in quenching experiments. The portion of photoreactivity that remains unquenched upon complete ^2E emission quenching has unanimously been assigned to the short-lived quartet state(s), formed in competition with prompt intersystem crossing to the longer-lived doublet during vibrational relaxation of Franck–Condon states [10–14].

Pulse studies of $Cr(NH_3)_5(CN)^{2+}$ and other am(m)ine complexes with conductivity monitoring of the products, have confirmed the unquenchable photochemistry to be "fast" or in the sub-nanosecond range, and the quenchable one "slow", its rate being indeed equal to that of ^2E decay [100].

For the latter, three hypotheses have been advanced: (1) direct doublet reaction,

(2) back intersystem crossing followed by quartet reaction and (3) crossing to a reactive ground-state intermediate. No uniform scheme appears to apply to all systems, though [10–14]. This still controversial matter is deferred to Sect. 7.1, and only the "chemical" aspects bearing on it are considered here. Some of the cyano-am(m)ines are well-suited for studies in this regard, owing to their relatively long-lived doublet emission combined with multiple photolysis modes.

Ammonia photoaquation of $Cr(NH_3)_5(CN)^{2+}$ is 73% quenchable by OH^- or $Cr(CN)_6^{3-}$: the *cis-/trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$ product ratio and the apparent activation energy for Φ_{NH_3} are the same for the quenched and unquenched reaction yields [101].

Likewise, 75% of each photoreaction of *trans*-$Cr(NH_3)_4(NCS)(CN)^+$ is quenched by $Cr(C_2O_4)_3^{3-}$, again denoting the same $NH_3:NCS^-:CN^-$ proportion for the quenchable and unquenchable component [77].

These findings point to a single precursor to all photochemistry, to say the least. For $Cr(NH_3)_5(CN)^{2+}$ a constant isomer ratio arising from different transition states may still be either accidental or due to chemical events subsequent to the photochemical events. For *trans*-$Cr(NH_3)_4(NCS)(CN)^{2+}$, instead, it is highly improbable that identical preferences in the cleavage of *three* distinct metal–ligand bonds be exhibited by states of different electronic configurations and equilibrium structures, such as $^4B_2/^4E$ (t_2^2e) and $^2A_1/^2B_1$ (t_2^3) or an intermediate deriving from the latter. The plausibility of pathway (2) for these species is corroborated by the activation energy for ^2E decay (Sect. 7.1 and Table 11) and by the reactivity entirely explainable by the quartet-related models.

A significant supplementary observation is that doublet quenching of $Cr(NH_3)(CN)_5^{2-}$ by $Co(sep)^{3+}$ in dmso leaves the two photosolvation modes entirely unquenched. Here, similarly to $Cr(CN)_6^{3-}$, back intersystem crossing is definitely precluded by the large quartet–doublet energy difference, so that loss of *both* NH_3 and CN^- must be concluded to originate in the lowest quartet state(s) prior to intersystem crossing [45].

The photochemistry of *trans*-$Cr(tn)_2(CN)_2^+$ is efficiently quenched by the photoproducts themselves. The long doublet lifetime of this complex makes the phenomenon particularly evident since the early photolysis stages [31]. In principle, such a complication may affect other systems with sufficiently long-lived doublets [101], and may well have been overlooked because of analytical inadequacy.

6.4 *Charge-transfer photochemistry*

Given the interest in the LF behaviour, the CT reactivity of Cr(III) has been, in general, rather neglected. Three complexes of the cyanoammine family have received attention from this point of view.

Irradiation of the UV band of $Cr(NH_3)_5(CN)^{2+}$, associated with the $t_2(Cr) \rightarrow \pi^*(CN)$ transition (Sect. 4.4), brings about a chemistry qualitatively and

TABLE 11

Doublet-state emission lifetimes and their temperature dependence

Complex[a]	Medium	τ_{77} (μs)	τ_{293} (μs)	E^{*b} (kJ mol^{-1})	Ref.
$Cr(NH_3)_5(CN)^{2+}$	H_2O^c		22	47	78
	dmf/EtOH	79			106
	dmso/H_2O	100			32
	dmso		35	55	78
	dmf		20	53	78
	tms		18	60	78
	solid		32		78
$Cr(ND_3)_5(CN)^{2+}$	D_2O^d		32	52	78
	dmso/D_2O	7460			32
trans-$Cr(NH_3)_4(CN)_2^+$	H_2O^e		40	28	78
	dmso		19	55	78
	dmf		10	36	78
	solid		66		78
cis-$Cr(NH_3)_4(CN)_2^+$	H_2O^e		26	27	78
	dmso		71	30	78
	dmf		33	25	78
	tms		93	53	78
	solid		78		78
trans-$Cr(NH_3)_4(NCS)(CN)^+$	H_2O^c		30	38	77
trans-$Cr(NH_3)_4(H_2O)(CN)^{2+}$	H_2O^c		1.1	55	78
trans-$Cr(NH_3)_4Cl(CN)^+$	H_2O^c		0.26	47	108
trans-$Cr(NH_3)_4F(CN)^+$	H_2O^c		0.26	46	108
cis-$Cr(NH_3)_4(dmso)(CN)^{2+}$	H_2O^c		10		78
trans-$Cr(en)_2(CN)_2^+$	H_2O^f		1^g		83
	dmso	210	1^g		83
cis-$Cr(en)_2(CN)_2^+$	H_2O^f		2^g		83
	dmso	200	9^g		83
cis-$Cr(D\text{-}en)_2(CN)_2^+$	dmso	3000	11^g		83
trans-$Cr(tn)_2(CN)_2^+$	H_2O		185		31
trans-$Cr(cyclam)(CN)_2^+$	H_2O^f		335^g	38^h	83
	D_2O		357^g		83
	dmso	355	330^g		83
	dmso/H_2O	500			29
	dmso/H_2O	361	361^i		68
trans-$Cr(D\text{-}cyclam)(CN)_2^+$	H_2O^f		1500^g	40^h	83
	dmso	3060	1650^g		83
	dmso/D_2O	3050			32
	dmso/D_2O	4645	1725^i		68
trans-Cr(tet*a*)$(CN)_2^+$	H_2O^f		395		29
	dmso/H_2O	560	460		29
	dmso/H_2O	380	379^i		68
trans-Cr(D-tet*a*)$(CN)_2^+$	dmso/D_2O	3040	1060^i		68
trans-$Cr([15]aneN_4)(CN)_2^+$	dmso/H_2O	278	190^i		68
cis-Cr(tet*b*)$(CN)_2^+$	dmso/H_2O	204	2.0^i	50	68

TABLE 11 (*continued*)

Complex[a]	Medium	τ_{77} (μs)	τ_{293} (μs)	E^{*}[b] (kJ mol^{-1})	Ref.
cis-Cr(D-tet*b*)$(CN)_2^+$	dmso/D_2O	1860	2.0[i]		32
cis-$Cr(bpy)_2(CN)_2^+$	dmso/H_2O	3600	0.1	34	26
Cr(tacn)$(CN)_3$	dmso/H_2O	402	6.1[i]		68
Cr(phen)$(CN)_4^-$	dmso/H_2O	4320	0.4[i]	33	26
$Cr(NH_3)(CN)_5^{2-}$	dmso		32		45
$(NH_3)_5Cr(\mu\text{-}NC)Co(CN)_5$[j]	H_2O[k]		1.9	40[l]	59
$[(NH_3)_5Cr(\mu\text{-}NC)]_2Ru(bpy)_2^{6+}$	dmso/H_2O	78			63
$[(NC)(cyclam)Cr(\mu\text{-}CN)]_2Ru(bpy)_2^{4+}$	H_2O[c]		260		66
	dmf		300		66
$(NC)(cyclam)Cr(\mu\text{-}CN)Cr(CN)_5^-$[m]	dmf		81		65

[a] D denotes perdeuteration of the N—H protons.

[b] The activation energies E^{*} refer to the higher-temperature range.

[c] 10^{-3} M $HClO_4$.

[d] pH 3.3.

[e] pH 5 (phthalate buffer).

[f] 5×10^{-3} M HNO_3.

[g] 295 K.

[h] Determined in the 320–350 K temperature interval [110].

[i] 298 K.

[j] Emission from the CrN_6 moiety.

[k] 0.02 M $HClO_4$.

[l] Apparent activation energy for the emission intensity.

[m] Emission from the CrC_5N moiety.

quantitatively identical with the LF one (Table 9), comprising the same isomer composition of products. This suggests virtually complete conversion of the MLCT state(s) to the LF manifold [99].

On the other hand, CT photolysis of *trans*-$Cr(NH_3)_4Cl(CN)^+$ raises Φ_{Cl^-} and Φ_{NH_3}, and reduces Φ_{CN^-} with respect to LF photolysis. In this case, the UV absorption is due to overlap of $t_2(Cr) \rightarrow \pi^*(CN)$ and $\pi(Cl) \rightarrow e^*(Cr)$ transitions. The relative yields for reaction and phosphorescence on CT and LF excitation, denote a photoactive LMCT state and, again, a photoinert MLCT one, with a 0.4 efficiency for CT → LF conversion [82]. Although the charge shift implies primary homolytic bond fission, the observed photoproducts are substitutional, as the unpaired electron would have essentially unit probability of being transferred from Cr(II) to $\dot{C}l$ before the fragments leave the solvent cage.

The CT spectrum of *trans*-$Cr(NH_3)_4(NCS)(CN)^+$ is dominated by the $\pi(NCS) \rightarrow e^*(Cr)$ absorption, and the processes following UV excitation are accounted for by the scheme [102]

$$\{Cr(NH_3)_4(CN)^+, H_2O, {}^{\bullet}NCS\} \begin{cases} \longrightarrow Cr(NH_3)_4(H_2O)(CN)^{2+} + NCS^- \\ \longrightarrow Cr(aq)^{2+} + 4NH_3 + CN^- + {}^{\bullet}NCS \end{cases} \tag{11}$$

Cr(II) scavenging indicates that the fragments now competitively escape the cage with or without back charge transfer to ${}^{\bullet}NCS$, the former path being favoured by the high reducing power of Cr(II). The Φ_{NCS^-} increase at shorter wavelengths (Table 9) is consistent with a radical-pair mechanism, whereby excess energy prevents primary recombination of the cage partners [102]. On the grounds that the quenchability of the various reactions is an inherent LF property, analysis of the CT and LF behaviours in the presence and in the absence of a quencher gives an efficiency of 0.6 for communication between CT and LF states [103].

Irradiation of MMCT bands of binuclear complexes also induces photoredox processes. Stimulation of the Fe(II)→Cr(III) transition of $(NH_3)_5Cr(\mu\text{-}NC)Fe(CN)_5^-$, generates $Fe(CN)_6^{3-}$. Stabilization of this product has been attributed to fast dissociation of the labile Cr unit of the Fe(II)–Cr(III) transient isomer, successfully competing with back electron transfer [57].

7. PHOTOPHYSICS

7.1 Doublet-state lifetimes

The general subject is broad and, of necessity, attention is mostly restricted to the cyanoam(m)ine species, although sometimes these have been studied in the context of larger groups of complexes. For the background and for detailed kinetic analyses of the processes involving the ^2E and $^4T_2$ states, reference is made to the excellent monographs by Kemp [104] and Forster [15,105].

Emission from the ^2E energy level (in O_h approximation) is ubiquitous for Cr(III) in low-temperature glasses but not in room-temperature solution. The relatively long-lived phosphorescence of the cyanoam(m)ines under the latter conditions, where photochemistry also takes place, renders these systems particularly informative on the excited-state dynamics. Table 11 groups the ^2E lifetimes at 77 and 293 K. The distinction is customary, as most complexes behave differently in the two temperature ranges: below 150–200 K the ^2E decay is nearly matrix- and temperature-independent, whereas at higher temperatures, specially in fluid solution, it becomes medium-sensitive and exhibits an Arrhenius dependence. The apparent activation energies for the latter are included in Table 11.

The ^2E state can, in principle, disappear through radiative (r) and non-radiative (nr) deactivation to the $^4A_2$ ground state, back intersystem crossing (bisc) to $^4T_2$, and chemical reaction (cr), so that its lifetime, τ, is given by

$$\tau^{-1} = k_r + k_{nr} + k_{bisc} + k_{cr} \tag{12}$$

7.1.1 Low-temperature emission

The radiative lifetime, $\tau_r = k_r^{-1}$, is typically in the ms time scale and is ordinarily assumed to be temperature- and environment-independent. It is approached more or less closely by the τ values at 77 K of perdeuterated am(m)ine complexes, which are virtually insensitive to the number of N–D bonds. Under these circumstances the k_{bisc} and k_{cr} paths are, in general, inhibited: in addition, the k_{nr} contribution is drastically reduced by deuteration, as no high-frequency N–H vibrations are available to mediate the excited-state relaxation. This is indeed the case for $Cr(ND_3)_5(CN)^{2+}$ [32] and the four $Cr(D{-}N)_4(CN)_2^+$ species [32,68,83]. Similar behaviour is observed in $Cr(bpy)_2(CN)_2^+$ and $Cr(phen)(CN)_4^-$, which do not possess H atoms in the vicinity of the d-electron density [32].

In proteo am(m)ine compounds, the low-temperature limiting lifetime is at least one order of magnitude shorter than in the deutero compounds and tends to decrease with increasing number of N–H bonds; cf. Table 11: macrocycles > en > NH_3. τ^{-1} is now taken as a good measure of k_{nr}: such bonds, in fact, provide high-frequency accepting modes for non-radiative relaxation, a weak coupling process because ^2E and $^4A_2$ have the same nuclear coordinates.

The cyanide ligand is a poor mediator of the k_{nr} path owing to the relatively low frequency (<2200 cm^{-1}) of its C–N vibrations [15]. Other factors being equal, the cyanoam(m)ines thus have the longest-lived 77 K emissions among similar acidoam(m)ines.

The doublet decay can as well be affected by the ^2E–$^4A_2$ energy gap and by the geometry of the polyamines [14,15]. An analysis of the τ_{77} values for the deuterated and undeuterated forms of a series of complexes comprising various cyanoam(m)ines and having different numbers of N–H oscillators, demonstrated that besides high-frequency intraligand motions, low-frequency Cr–ligand skeletal vibrations contribute significantly to k_{nr}. The geometry dependence was accounted for by this second mode, the efficacy of which is apparently increased by distorted or strained coordinations [32].

7.1.2 Temperature-dependent ^2E deactivation

In the temperature-sensitive range there is a wide variety of lifetimes and activation parameters, influenced by the ligand composition and the solvent. The rapid decrease of τ in this region has been attributed to the intervention of one or more of the following thermally activated processes: (a) back intersystem crossing (k_{bisc}) to the short-lived, unstable $^4T_2$ state, (b) direct ^2E reaction (k_{cr}) and (c) enhancement of non-radiative relaxation, described by a $k_{nr}(T)$ rate constant added to the limiting low-temperature term k_{nr}^0. The choice of the appropriate rate-determining pathway(s) has long been debated and has prompted numerous studies of structural and environmental effects on the ^2E decay [11,14,15,26,68,78,83,106,107,110].

Absolute τ values alone, without the supplement of their activation parameters, should be interpreted cautiously. The medium dependence of $\ln(\tau^{-1}) = \ln A - E^*/RT$

for a series of $Cr(NH_3)_4X(CN)^{z+}$ ions [78] has shown that variations in ln A and E^* greatly exceed those of $\ln(\tau^{-1})$. That is, several-fold changes in τ can arise from balancing of as much as 10^6-fold variations in A and nearly matching opposite variations in $\exp(E^*/RT)$. For a given complex in different solvents there are cases where τ increases while E^* decreases and vice versa (Table 11).

The linearity of Arrhenius plots suggests that, usually, a single process dominates, although sometimes this is unwarranted by the small temperature intervals explored. In some instances, two-term Arrhenius functions appear more adequate to fit the data [15]. Also, the linear relationship between E^* and $\Delta S^{\neq}$ in terms of transition-state theory (Barclay–Butler plot) obeyed by related compounds in various media, has been regarded as indicative of the same decay route for the whole group, whatever the route [78,104].

As to the actual deactivation channel, there is sufficient evidence that no uniform mechanism applies to all Cr(III) species, but experimental distinction of possibilities (a), (b) and (c) has, in general, been problematic. In particular, the data for the cyanoam(m)ine complexes are often compatible with more than one interpretation, and this survey is necessarily limited to comparison with the various models that have been proposed.

(*a*) *Back intersystem crossing.* Indications as to the occurrence of bisc are sought by comparing E^* with the $^4T_2$–^2E energy gap. It is conventional to consider this path improbable when the gap is larger than ca. 40 kJ mol^{-1}, as is the case for CrN_6 coordination [15]. For a series of hexaamine species, no parallel was, in fact, found between E^* and the $^4T_2$–^2E separation [106]. The wider gap of the cyanoam(m)ines due to the spectrochemical and nephelauxetic effects of CN^- would, therefore, be even more preclusive to this route. Also, for the latter family, no such energy relationship is apparent [78,106]. The E^* values for the NH_3 complexes of Table 11 in a given medium are higher for monocyano than for dicyano species, contrary to expectations based on bisc [78]. It should be noted, however, that the different equilibrium structures of the states involved in bisc may introduce factors obscuring the energy correlation. The $^4T_2$–^2E gap can only be evaluated indirectly from the spectra; moreover, different contributions of solvent reorganization to E^* may alter "pure" state energies.

In contrast with the above inferences stand the quenching results with $Cr(NH_3)_5(CN)^{2+}$ [101] and *trans*-$Cr(NH_3)_4(NCS)(CN)^+$ [77] (Sect. 6.3): the same product proportions for prompt $^4T_2$ photochemistry and for the part of chemically dissipated energy that traverses ^2E, are consistent with bisc followed by delayed $^4T_2$ reaction.

The bisc hypothesis was examined in relation to the exceptionally large τ_{293} values of the photoinert *trans*-Cr(cyclam)$(CN)_2^+$ (335 μs) [83] and *trans*-Cr(teta)$(CN)_2^+$ ions (395 μs) [29], compared with that (1 μs) of the photolabile *trans*-$Cr(en)_2(CN)_2^+$ homologue [83]. The lack of reactivity from $^4T_2$ would determine an intersystem crossing efficiency, η_{isc}, close to unity (as experimentally verified, vide infra), with a consequent drastic reduction of $k_{\text{bisc}} = (1 - \eta_{\text{isc}})k$, where k is the mechanistic rate constant [15]. However, the observation that not all photoinert macrocyclic systems have long-lived room-temperature emissions, suggests other relaxation channels for complexes of this type [14].

(*b*) *Doublet-state reaction.* Relevant to the possibility of ^2E decay via direct reaction (k_{cr}) are the empirical emission rules formulated by Walters and Adamson [107], relating τ_{293} to the photoreactivity. The rule applicable to mixed-ligand complexes predicts "a relatively short lifetime ($\tau < 1$ μs) if that ligand which is preferentially substituted in the thermal reaction lies on the weak field axis".

Rationalization of the rules implies a chemical control of the ^2E lifetime. When the preferred photoreaction mode is the same as the ground-state mode, it would be facilitated by a similar substitution mechanism because of the electronic and geometric similarities of ^2E and $^4A_2$, and k_{cr} would be large. Antithermal photoreactions would then be associated with smaller k_{cr} values.

The *trans*-$Cr(NH_3)_4X(CN)^{z+}$ series where $X = NH_3$, CN^-, NCS^-, H_2O, Cl^- and F^- (Table 11), conforms nicely to the predicted pattern [108], as do a number of other acidoam(m)ines [107]. In all cases, the thermally labile ligands are on the tetragonal axis, which is the strong-field one for $X = NH_3$, CN^- and NCS^-, and the weak-field one for $X = Cl^-$ and F^-. In the former group, the lifetimes are, in fact, two orders of magnitude larger than in the latter [77,78,108]. The ligand-field situation and the τ_{293} value for $X = H_2O$ [78] are consistently in between. The rule is again predictive for the two *cis*-$Cr(NH_3)_4X(CN)^{z+}$ with $X = CN^-$ and dmso [78].

In this framework, the long-lived emission of the *trans*-$CrN_4(CN)_2^+$ macrocyclic complexes would be justified by the absence of direct ^2E reaction [29,83].

(*c*) *Crossing to a ground-state intermediate.* An alternative thermally activated pathway has been proposed that would partially or totally account for $k_{\text{nr}}(T)$ when bisc is precluded, namely, crossing to the potential energy surface of a distorted intermediate in its electronic ground state [14]. In consideration of the substitutional behaviour of Cr(III), a seven-coordinate intermediate formed by solvent association is plausible: a transient chemical species has indeed been detected on doublet decay of *cis*-$Cr(cyclam)(NH_3)_2^{3+}$ [109]. In photolabile systems, such an intermediate would decompose to products. The picture includes the compounds made photoinert by the constraints of macrocyclic or cage-type ligands: in these cases, solvent expulsion from the intermediate would result in no net reaction. The wide range of emission rates for the unreactive complexes was taken to indicate that there are macrocycle stereochemistries (presumably those trigonally distorted) that favour relaxation, while others do not [68,106]. This theory thus relates the shorter lifetimes to bisc and, when this is energetically prevented, to steric factors promoting appropriate molecular vibrations. The magnitude of τ would not necessarily be connected with photolability.

For the centrosymmetric *trans*-$Cr(cyclam)(CN)_2^+$ complex [83] and its teta analog [29] the temperature-independent regime and the prolongation of τ upon perdeuteration extend up to ca. 300 K. This unique property was attributed to blocking of the thermally activated relaxation channel by the restriction exerted on the nuclear motions by the equatorial amine rings [106,110]. No such restriction is believed to operate in the shorter-lived and non-centric *cis*-Cr(tet*b*)$(CN)_2^+$ ion, which exhibits a "normal" temperature-dependent solution lifetime [68].

In conclusion, while there continues to be debate on the whole matter, it seems possible to recognize some regularities. k_{bisc} is likely to be rate-determining in CrN_5X^{2+} and $CrN_4X_2^+$ compounds with lower-field ligands such as $X = Cl^-$ or Br^-, the short lifetimes of which appear insensitive to the polyamine stereochemistry [106]. At least for the macrocyclic cyanoamines, the ground-state-intermediate model satisfactorily explains the variety of ambient lifetimes. Concerning the cyano complexes with NH_3 or simple amine ligands, the contention is that bisc is hindered on energetic grounds, so that reactive deactivation would take place from ^2E, whether directly or via an intermediate: the lack of steric factors does not enable distinction between the k_{cr} and $k_{\mathrm{nr}}(T)$ routes, but the apparent correlation of τ with thermal lability is congruent with the former.

The positive volumes of activation for the room-temperature ^2E decay rates of $Cr(NH_3)_5(CN)^{2+}$ and *trans*-Cr(cyclam)$(CN)_2^+$, among those of other Cr(III) am(m)ines, although not diagnostic, were considered more supportive of chemical reaction from the doublet state than via bisc [111].

Some aspects are still elusive. For example, the quenching behaviour is apparently inconsistent with the reactivity somehow originating in ^2E. The finding that the quenchable fraction of products appears with the same lifetime as for emission decay [100] cannot discriminate between k_{bisc} and either k_{cr} or $k_{\mathrm{nr}}(T)$. However, the quenchable photochemistries of $Cr(NH_3)_5(CN)^{2+}$ [101] and *trans*-$Cr(NH_3)_4(NCS)(CN)^+$ [77], like the unquenchable photochemistries, bear the imprint of the antibonding character of $^4T_2$, which is electronically and structurally quite different from ^2E: therefore, in some of the high-field complexes, bisc cannot be completely ruled out.

In regard to this point, the idea has recently been advanced that, in photoreactive systems, the barrier to bisc may be reduced significantly with respect to the estimated spectroscopic value by a strong interaction of the quartet excited state with the nucleophilic solvent. The distortion of the $^4T_2$ potential energy surface along a coordinate for chemical reaction would cause a lower-lying intersection of the doublet and quartet surfaces [112]. Of course, all the above uncertainties remain because the intimate mechanism of each postulated process is not yet known.

Other factors, in addition to the structural and environmental factors, may affect the luminescence decay. Magnetic perturbations have been investigated in the *trans*-$CrN_4(CN)_2^+$ complexes with $N_4 = (NH_3)_4, (en)_2$, cyclam and [15]aneN_4. Under a 6 T magnetic field, the emission lifetimes are a few percent shorter than under zero field, both at 77 K and at 298 K. The magnetodynamic effect was ascribed to field-induced changes in the population of the Zeeman doublet sublevels, in addition to changes in their intrinsic relaxation rates [81].

7.2 Intersystem crossing

Although the efficiency of the ${}^4T_2 \rightarrow {}^2E$ relaxation process is important to assess the role of the two lowest excited states of different spin multiplicity, it has been measured in only a few Cr(III) complexes [15]: some recent data pertain to cyanoam(m)ines.

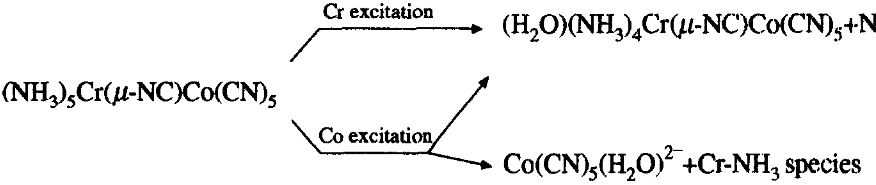
The method of comparing the direct and sensitized emission intensities gave an intersystem crossing yield $\eta_{isc} = 1.0 \pm 0.1$ for *trans*-$Cr(cyclam)(CN)_2^+$ in ambient-temperature aqueous solution [66].

In another study, the less conventional technique of pulsed photoacoustic microcalorimetry was applied under the same conditions to this complex and to the analogous *trans*-$Cr([15]aneN_4)(CN)_2^+$ ion. The approach was to monitor the heat released during ${}^4T_2$ relaxation and to compare it with the energy of excitation to this state and the energy of the eventually produced ${}^2E$ state. The η_{isc} values were found to be 1.11 ± 0.10 and 1.08 ± 0.05, respectively [113]. Photoinert species having long ${}^2E$ lifetimes appear to undergo this process much more efficiently than other Cr(III) systems [15]. Prompt ${}^4T_2$ photochemistry (in addition to possible ${}^4T_2 \rightarrow {}^4A_2$ non-radiative deactivation) obviously accounts for the reduction of η_{isc} in the latter.

7.3 Energy migration in CN-bridged polynuclear complexes

Several homo- and heteropolynuclear species have been designed to study intramolecular energy transfer between covalently bound metal centres. In such species, each bonded component essentially retains its original properties, so that the label "supermolecules" applies. The matter has been recently surveyed [114,115]: considered here are, naturally, the systems involving cyano-linked Cr(III)-am(m)ine units. The fairly long-lived and low-lying ${}^2E$ emitting state of Cr(III) makes these units suitable as energy acceptors, particularly in room-temperature solution.

Aqueous $(NH_3)_5Cr(\mu\text{-}NC)Co(CN)_5$ has been investigated on selective irradiation of the well-separated low-energy LF bands of the Cr and Co fragments, i.e. by initially producing the respective ${}^4T_2$ and ${}^1T_1$ states. Cr(III) excitation (436 nm) results in NH_3 loss ($\Phi = 0.21$) and phosphorescence from the CrN_6 centre (685 nm, Table 6); Co(III) excitation (313 nm) leads to CN-bridge cleavage ($\Phi = 0.08$) and, again, to NH_3 aquation ($\Phi = 0.16$) plus CrN_6 emission (eqn. (13)).



$$\begin{tikzcd}
 & (H_2O)(NH_3)_4Cr(\mu\text{-}NC)Co(CN)_5 + NH_3 \\
(NH_3)_5Cr(\mu\text{-}NC)Co(CN)_5 \arrow[ur, "\text{Cr excitation}"] \arrow[dr, "\text{Co excitation}"'] \arrow[ur, bend right, "\text{Co excitation}"'] & \\
 & Co(CN)_5(H_2O)^{2-} + Cr\text{-}NH_3 \text{ species}
\end{tikzcd} \qquad (13)$$

On 313 nm irradiation, the cleavage quantum yield is ca. 25% of that for CN^- release in the mononuclear $Co(CN)_6^{3-}$ model, while the yields of NH_3 aquation and CrN_6 emission are ca. 75% of the values for direct irradiation of the Cr component. Intramolecular Co → Cr energy transfer was thus proven. The proportion of Co(III) quenching and Cr(III) sensitization, and the symmetry requirements favour $^1T_1/^3T_1(Co) \rightarrow {}^4T_2(Cr)$ transfer among the energetically possible pathways [59].

Energy migration has been shown to occur from Ru(II) to the Cr(III) centres of trinuclear $[(NH_3)_5Cr(\mu\text{-}NC)]_2Ru(bpy)_2^{6+}$. In dmso/$H_2O$ glass at 77 K, quenching of the phosphorescence of the $Ru(bpy)_2^{2+}$ MLCT triplet is, in fact, accompanied by emission from the Cr(III) doublet (Table 6) [63]. The phenomenon becomes undetectable at room temperature.

This process also takes place within the related dinuclear ion $(NH_3)_5Cr(\mu\text{-}NC)Ru(bpy)(CN)_3^+$, where the non-bridging CN^- groups are sensitive to second-sphere interactions. The gap between the Ru(II)-donor triplet and the Cr(III)-acceptor doublet can be thus modified by solvent effects or protonation, in order to investigate the driving-force requirements of the energy transfer step [116].

The Cr-C bound *trans*-$Cr(cyclam)(CN)_2^+$ unit, a photoinert and efficient emitter (Sect. 7.1), has been incorporated in various polynuclear species. The spectrum of $[(NC)(cyclam)Cr(\mu\text{-}CN)]_2Ru(bpy)_2^{4+}$ is dominated by the intense MLCT band of the $Ru(bpy)_2^{2+}$ moiety. In room-temperature aqueous medium, absorption of visible light by this moiety leads to strong ($\Phi = 5.3 \times 10^{-3}$) and long-lived ($\tau = 260\ \mu s$) phosphorescence from Cr(III) only. The chromophore–luminophore exchange energy-transfer occurs in the sub-nanosecond time scale with unit efficiency [66].

Differently from the previous cases, LF spectral overlap in the Cr(III)–Cr(III) system *trans*-$(NC)(cyclam)Cr(\mu\text{-}CN)Cr(CN)_5^-$ [65] does not enable excitation of a single metal centre. However, regardless of the exciting wavelength, emission in dmf occurs exclusively from the $Cr(CN)_5(NC)^{3-}$ subunit, as identified by comparison (Tables 6 and 11) with that of the model compound $Cr(NH_3)(CN)_5^{2-}$ [45]. This is, again, indicative of efficient energy transfer from the higher-lying ^2E state of the Cr-cyclam fragment to the lower-lying ^2E state of the Cr-cyano fragment. On the assumption of a unitary $^4T_2 \rightarrow {}^2E$ intersystem crossing yield for the former fragment (as is the case for unbound *trans*-$Cr(cyclam)(CN)_2^+$ [66]), the differences between the excitation and absorption spectra of the dinuclear complex suggest a 0.1–0.2 efficiency for intersystem crossing within the $Cr(CN)_5(NC)^{3-}$ unit [65].

An interesting extension of the above results is the evidence for a two-step energy transfer along the —Ru—Cr—Cr chains of the pentanuclear complex $[(CN)_5Cr(\mu\text{-}NC)Cr(cyclam)(\mu\text{-}CN)]_2Ru(bpy)_2$, formed in dmf solution but not isolable. Upon connection of $-Cr(CN)_5^{2-}$ groups to $[(NC)(cyclam)Cr(\mu\text{-}CN)]_2Ru(bpy)_2^{4+}$, the 727 nm emission of the Cr-cyclam centre [66] disappears, giving place to 778 nm emission from the terminal $Cr(CN)_5(NC)^{3-}$ centres [65].

7.4 *Bimolecular interactions*

The quenching of the luminescent ^2E state of some Cr(III) cyanoam(m)ine compounds by other complexes under ambient conditions has already been mentioned in Sect. 6.3 [31,45,77,101]. Evidence that the interaction of $Cr(NH_3)_5(CN)^{2+}$ with $Cr(CN)_6^{3-}$ is one of excitation energy transfer was provided by the sensitized emission of the hexacyanochromate(III) ion in dmf solution [101].

Intermolecular processes have been studied where the Cr(III) doublets function as energy acceptors. $Cr(NH_3)_5(CN)^{2+}$ and *trans*-$Cr(cyclam)(CN)_2^+$, as well as other am(m)ine and acidoam(m)ine species, are able to quench the MLCT phosphorescent triplet states of $Ru(bpy)_3^{2+}$ and $Ru(bpy)_2(CN)_2$ in aqueous solution [117]. Since, in the cyanoam(m)ines, the excited-quartet energy is relatively high, the spectral overlap with the Ru(II) emission is very small and only the Cr(III) doublets are accessible for energy transfer. The quenching rates were found to be much smaller than the diffusion limit and to increase with the energy gap between the donor and acceptor levels. The interaction was described as vibronic tunnelling between nested, or weakly coupled, reactant and product potential surfaces, and the low efficiencies were attributed to the very small donor-localized nuclear displacements accompanying the process. The enhanced quenching by acidoam(m)ine complexes with a lower-lying $^4T_2$ state, hence with an appreciable spectral overlap, was then related to the competitive contribution of a strongly coupled quenching channel leading to such a state [117].

REFERENCES

1 C.S. Garner and D.A. House, Transition Met. Chem., 6 (1970) 59.
2 L.S. Forster, Transition Met. Chem., 5 (1969) 1.
3 J.R. Perumareddi, Coord. Chem. Rev., 4 (1969) 73.
4 A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1984, Chap. 6 and references cited therein.
5 D.J. Hodgson, in R.D. Willett, D. Gatteschi and O. Kahn (Eds.), Magneto-Structural Correlations in Exchange Coupled Systems, Reidel, Dordrecht, 1985, p 497.
6 J.O. Edwards, F. Monacelli and G. Ortaggi, Inorg. Chim. Acta, 11 (1974) 47.
7 T.W. Swaddle, Coord. Chem. Rev., 14 (1974) 217.
8 D.A. House, Coord. Chem. Rev., 23 (1977) 223.
9 L. Mønsted and O. Mønsted, Coord. Chem. Rev., 94 (1989) 109.
10 E. Zinato, in A.W. Adamson and P.D. Fleischauer (Eds.), Concepts of Inorganic Photochemistry, Wiley, New York, 1975, Chap. 4.
11 A.D. Kirk, Coord. Chem. Rev., 39 (1981) 225.
12 B.R. Hollebone, C.H. Langford and N. Serpone, Coord. Chem. Rev., 39 (1981) 181.
13 L.G. Vanquickenborne and A. Ceulemans, Coord. Chem. Rev., 48 (1983) 157.
14 J.F. Endicott, T. Ramasami, R. Tamilarasan, R.B. Lessard and G.R. Brubaker, Coord. Chem. Rev., 77 (1987) 1.
15 L.S. Forster, Chem. Rev., 90 (1990) 331.
16 J.E. Vaughn, Coord. Chem. Rev., 39 (1981) 265.

17 J. Springborg, Adv. Inorg. Chem., 32 (1988) 55.
18 A.G. Sharpe, The Chemistry of Cyano Complexes of the Transition Metals, Academic Press, London, 1976.
19 W.P. Griffith, Coord. Chem. Rev., 17 (1975) 177.
20 B. Sieklucka, Prog. React. Kinet., 15 (1989) 175.
21 S. Kaizaki, J. Hidaka and Y. Shimura, Bull. Chem. Soc. Jpn., 48 (1975) 902.
22 A.D. Kirk and G.B. Porter, Inorg. Chem., 19 (1980) 445.
23 P. Riccieri and E. Zinato, Inorg. Chem., 20 (1981) 3722.
24 R.D. Archer, Coord. Chem. Rev., 4 (1969) 243.
25 Z. Chen, M. Cimolino and A.W. Adamson, Inorg. Chem., 22 (1983) 3035.
26 C.K. Ryu and J.F. Endicott, Inorg. Chem., 27 (1988) 2203.
27 P. Riccieri and E. Zinato, Inorg. Chem., 19 (1980) 853.
28 N.A.P. Kane-Maguire, J.A. Bennett and P.K. Miller, Inorg. Chim. Acta., 76 (1983) L123.
29 N.A.P. Kane-Maguire, K.C. Wallace, D.P. Cobranchi, J.M. Derrick and D.G. Speece, Inorg. Chem., 25 (1986) 2101.
30 S. Kaizaki and H. Takemoto, Inorg. Chem., 29 (1990) 4960.
31 A.D. Kirk and S.R.L. Fernando, Inorg. Chem., 31 (1992) 656.
32 C.K. Ryu, R.B. Lessard, D. Lynch and J.F. Endicott, J. Phys. Chem., 93 (1989) 1752.
33 N.E. Dixon, G.A. Lawrance, P.A. Lay and A.M. Sargeson, Inorg. Chem., 23 (1984) 2940.
34 M. Perkovic and G. Ferraudi, Inorg. Chim. Acta, 189 (1991) 55.
35 Y. Sakabe and Y. Matsumoto, Inorg. Chem., 24 (1985) 2119.
36 A.D. Kirk and C. Namasivayam, Inorg. Chem., 27 (1988) 1095.
37 B.G. Gafford, C. O'Rear, J.H. Zhang, C.J. O'Connor and R.A. Holwerda, Inorg. Chem., 28 (1989) 1720.
38 P. Riccieri and E. Zinato, Polyhedron, 11 (1992) 71.
39 P. Riccieri and E. Zinato, Inorg. Chim. Acta, 177 (1990) 147.
40 A.P. Sattelberger, D.D. Darsow and W.B. Schaap, Inorg. Chem., 15 (1976) 1412.
41 Y. Sakabe, Inorg. Chim. Acta, 168 (1990) 237.
42 Y. Sakabe and H. Ogura, Inorg. Chim. Acta, 189 (1991) 225.
43 E. Zinato, P. Riccieri and M. Prelati, Inorg. Chem., 20 (1981) 1422.
44 P. Riccieri and E. Zinato, Inorg. Chem., 22 (1983) 2305.
45 P. Riccieri and E. Zinato, Inorg. Chem., 29 (1990) 5035.
46 J. Ribas, J. Casabó, M. Serra and J.M. Coronas, Inorg. Chim. Acta, 36 (1979) 41.
47 J. Ribas, J. Casabó, M. Monfort, M.L. Alvarez and J.M. Coronas, J. Inorg. Nucl. Chem., 42 (1980) 707.
48 J. Ribas, M. Serra, A. Escuer and J.M. Coronas, J. Inorg. Nucl. Chem., 43 (1981) 3113.
49 M. Corbella, M. Serra, L. Martinez-Sarrion and J. Ribas, Thermochim. Acta, 57 (1982) 283.
50 J. Ribas, M. Monfort and J. Casabó, Transition Met. Chem. (Weinheim), 9 (1984) 407.
51 M. Corbella, M. Monfort and J. Ribas, Z. Anorg. Allg. Chem., 543 (1986) 233.
52 M. Corbella, S. Alvarez and J. Ribas, Inorg. Chim. Acta, 121 (1986) 13.
53 (a) M. Serra, A. Escuer, J. Ribas, M.D. Baro and J. Casabó, Thermochim Acta, 56 (1982) 183.
  (b) M. Serra, A. Escuer, J. Ribas and M.D. Baro, Thermochim. Acta, 64 (1983) 237.
  (c) M. Monfort, M. Serra, A. Escuer and J. Ribas, Thermochim. Acta, 69 (1983) 397.
  (d) J. Ribas, M. Serra, A. Escuer and M.D. Baro, Thermochim. Acta, 80 (1984) 103.
  (e) M. Serra, A. Escuer, M. Monfort and J. Ribas, Thermochim. Acta, 92 (1985) 493.
54 M. Johda, M. Suzuki and A. Uehara, Bull. Chem. Soc. Jpn., 62 (1989) 738.
55 A. Uehara, S. Terabe and R. Tsuchiya, Inorg. Chem., 22 (1983) 2864.
56 J. Ribas, A. Escuer and M. Monfort, Inorg. Chem., 24 (1984) 1874.

57 A. Vogler, A.H. Osman and H. Kunkely, Inorg. Chem., 26 (1987) 2337.
58 J. Ribas, M. Serra and A. Escuer, Transition Met. Chem. (Weinheim), 9 (1984) 287.
59 N.A.P. Kane-Maguire, M.M. Allen, J.M. Vaught, J.S. Hallock and A.L. Heatherington, Inorg. Chem., 22 (1983) 3851.
60 J. Ribas, J.M. Juliá, X. Solans, M. Font-Altaba, A. Isalgué and X. Tejada, Transition Met. Chem. (Weinheim), 9 (1984) 57.
61 J. Ribas, M.L. Martinez, M. Serra, M. Monfort, A. Escuer and N. Navarro, Transition Met. Chem. (Weinheim), 8 (1983) 87.
62 R. Billing and A. Hennig, J. Photochem. Photobiol. A, 63 (1992) 15.
63 Y. Lei, T. Buranda and J.F. Endicott, J. Am. Chem. Soc., 112 (1990) 8820.
64 J. Glerup and H. Weihe, Acta Chem. Scand., 45 (1991) 444.
65 C. Chiorboli, C.A. Bignozzi, M.T. Indelli, M.A. Rampi and F. Scandola, Coord. Chem. Rev., 111 (1991) 267.
66 C.A. Bignozzi, O. Bortolini, C. Chiorboli, M.T. Indelli, M.A. Rampi and F. Scandola, Inorg. Chem., 31 (1992) 172.
67 A.W. Hemmings, J.N. Lisgarten, R.A. Palmer and D.M. Gazi, Acta Crystallogr. Sect. C, 46 (1990) 205.
68 R.B. Lessard, M.J. Heeg, T. Buranda, M.W. Perkovic, C.L. Schwarz, Y. Rudong and J.F. Endicott, Inorg. Chem., 31 (1992) 3091.
69 Y. Sakabe, H. Sakaguchi, H. Takayanagi, H. Ogura and Y. Iitaka, Inorg. Chim. Acta, 183 (1991) 97.
70 U. Sakaguchi, K. Tomioka and H. Yoneda, Inorg. Chim. Acta, 101 (1985) 23.
71 V. Bertolasi, C.A. Bignozzi and F. Scandola, unpublished results 1992, as cited in ref. 66.
72 A. Whuler, C. Brouty, P. Spinat and P. Herpin, Acta Crystallogr. Sect. B, 33 (1977) 2877.
73 A. Heatherington, Su Min Oon, R. Vargas and N.A.P. Kane-Maguire, Inorg. Chim. Acta, 44 (1980) L279.
74 M.N. Hughes and W.R. McWhinnie, J. Chem. Soc. A, (1967) 592.
75 C.F.C. Wong and A.D. Kirk, Can. J. Chem., 53 (1975) 3388.
76 C.K. Poon and C.M. Che, Inorg. Chem., 20 (1981) 1640.
77 P. Riccieri, E. Zinato and A. Damiani, Inorg. Chem., 26 (1987) 2667.
78 E. Zinato, A.W. Adamson and P. Riccieri, J. Phys. Chem., 89 (1985) 839.
79 R. Dannöhl-Fickler, H. Kelm and F. Wasgestian, J. Lumin., 10 (1975) 103.
80 W. Tuszynski and E. Strauss, J. Lumin., 40–41 (1988) 276.
81 S. Ronco, M. Perkovic, G. Ferraudi and M. Cozzi, Chem. Phys., 162 (1992) 95.
82 P. Riccieri, E. Zinato and A. Damiani, Inorg. Chem., 27 (1988) 3755.
83 N.A.P. Kane-Maguire, W.S. Crippen and P.K. Miller, Inorg. Chem., 22 (1983) 696, 2972.
84 J.J. Alexander and H.B. Gray, J. Am. Chem. Soc., 90 (1968) 4260.
85 A. Vogler, A.H. Osman and H. Kunkely, Coord. Chem. Rev., 64 (1985) 159.
86 P. Riccieri and E. Zinato, Inorg. Chem., 24 (1985) 441.
87 P. Riccieri and E. Zinato, unpublished results, 1992.
88 D.K. Wakefield and W.B. Schaap, Inorg. Chem., 8 (1969) 512.
89 D.K. Wakefield and W.B. Schaap, Inorg. Chem., 10 (1971) 306.
90 J.M. Pratt and R.G. Thorp, Adv. Inorg. Chem. Radiochem., 12 (1969) 375.
91 F.R. Hartley, Chem. Soc. Rev., 2 (1973) 163.
92 J.P. Birk and J.H. Espenson, Inorg. Chem., 7 (1968) 991.
93 S.N. Frank and F.C. Anson, Inorg. Chem., 11 (1972) 2938.
94 J.P. Birk and J.H. Espenson, J. Am. Chem. Soc., 90 (1968) 1153.
95 A.W. Adamson, J. Phys. Chem., 71 (1967) 798.
96 J.I. Zink, J. Am. Chem. Soc., 94 (1972) 8039; Mol. Photochem., 5 (1973) 151; Inorg. Chem., 12 (1973) 1957; J. Am. Chem. Soc., 96 (1974) 4464.

97 M. Wrighton, H.B. Gray and G.S. Hammond, Mol. Photochem., 5 (1973) 165.
98 L.G. Vanquickenborne and A. Ceulemans, Inorg. Chem., 18 (1979) 897.
99 P. Riccieri and E. Zinato, Inorg. Chem., 19 (1980) 3279.
100 W.L. Waltz, J. Lilie and S.H. Lee, Inorg. Chem., 23 (1984) 1768.
101 E. Zinato, A.W. Adamson, J.L. Reed, J.P. Puaux and P. Riccieri, Inorg. Chem., 23 (1984) 1138.
102 J.F. Endicott, in A.W. Adamson and P.D. Fleischauer (Eds.), Concepts of Inorganic Photochemistry, Wiley, New York, 1975, Chap. 3.
103 P. Riccieri, E. Zinato and A. Damiani, Inorg. Chem., 28 (1989) 4506.
104 T.J. Kemp, Prog. React. Kinet., 10 (1980) 301.
105 L.S. Forster, Adv. Photochem., 16 (1991) 215.
106 R.B. Lessard, J.F. Endicott, M.W. Perkovic and L.A. Ochrymowycz, Inorg. Chem., 28 (1989) 2574.
107 R.T. Walters and A.W. Adamson, Acta Chem. Scand. Ser. A, 33 (1979) 53.
108 E. Zinato and P. Riccieri, Coord. Chem. Rev., (1993) in press.
109 W.L. Waltz, S.H. Lee, D.A. Friesen and J. Lilie, Inorg. Chem., 27 (1988) 1132.
110 J.F. Endicott, R. Tamilarasan and R.B. Lessard, Chem. Phys. Lett., 112 (1984) 381.
111 S.H. Lee, W.L. Waltz, D.R. Demmer and R.T. Walters, Inorg. Chem., 24 (1985) 1531.
112 A.D. Kirk and H.U. Güdel, Inorg. Chem., 31 (1992) 4564.
113 X. Song and J.F. Endicott, Inorg. Chem., 30 (1991) 2214.
114 F. Scandola, M.T. Indelli, C. Chiorboli and C.A. Bignozzi, Top. Curr. Chem., 158 (1990) 73.
115 V. Balzani and F. Scandola, Supramolecular Photochemistry, Horwood, New York, 1991, Chap. 6.
116 M.A. Rampi, L. Checchi and F. Scandola, unpublished results, as cited in refs. 114 and 115.
117 R. Tamilarasan and J.F. Endicott, J. Phys. Chem., 90 (1986) 1027.